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# ACID DEPOSITION PROGRAM

## PROGRESS REPORTS (1991-92)





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**ACID DEPOSITION PROGRAM PROGRESS REPORTS (1991-92)**

Submitted by

**ENVIRONMENTAL RESEARCH & ENGINEERING DEPARTMENT  
ALBERTA RESEARCH COUNCIL (ARC)**

**STANDARDS & APPROVALS  
ENVIRONMENTAL ASSESSMENT  
WASTES & CHEMICALS DIVISIONS  
ALBERTA ENVIRONMENTAL PROTECTION (AEP)**

**AIR ANALYSIS & RESEARCH BRANCH  
AIR & WASTE MANAGEMENT  
ALBERTA ENVIRONMENTAL CENTRE (AEC)**

Submitted to

**ACID DEPOSITION MANAGEMENT COMMITTEE  
ALBERTA ENVIRONMENTAL CENTRE  
ALBERTA ENVIRONMENTAL PROTECTION**

**Principal Investigators**

**L. Cheng, ARC  
R. Angle, AEP  
E. Peake, ARC  
S. Abboud, ARC  
L. Turchenek, ARC  
G. Lutwick, AEP  
H. Bertram, AEC**

**Compiled by**

**Nirmal C. Das, AEC**

**August, 1993**



## DISCLAIMER

This report is a compilation of a number of reports produced under the "Acid Deposition Program". The program was jointly funded by the Alberta Environmental Protection Department and the Alberta Research Council, and was managed by the Alberta Environmental Centre. The contents of the report do not necessarily reflect the views of the Alberta Environmental Centre and no official endorsement should be inferred. This report was peer-reviewed by the AEC and AES (Atmospheric Environment Service, Environment Canada) staff.

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## EXECUTIVE SUMMARY

(1991-92)

This report documents the progress and results achieved during 1991-92, under the Acid Deposition Program. Several projects were initiated under the program to achieve certain specific goals and objectives, which are described in the "Introduction" part of the report.

Under the data management project, an "Air Information System" has been established at the Environmental Assessment Division. A consulting firm (Coopers & Lybrand) was hired to perform the data base development for the system. The system is capable of storing and handling all acid deposition and air quality monitoring data. No written report was submitted on the information system. Designing of an emission inventory system was originally planned, but was not pursued, instead, Environment Canada's "Residual Discharge Information System (RDIS)" was adopted.

By using "Regional Lagrangian Model of Air Pollution (RELMAP)", an estimate of sulphur loadings in Alberta was generated. Application of this model predicted maximum ground level  $\text{SO}_2$  and  $\text{SO}_4^{=}$  concentrations in Edson and the Fort McMurray area, and maximum total sulphur deposition in the Whitecourt-Hinton area. Maximum dry deposition of  $\text{SO}_2$  was detected in Fort McMurray and the foothills region of the province. Another model, the Acid Rain Mesoscale Model (ARM3) was also applied in predicting the acidic deposition, but was found to be unsuitable for impact assessment at large distances downwind. However, for a single source and at short distances, ARM3 could be a useful model.

The objective of the soils component of the research program was to improve the capability in predicting the long term response of soils in Alberta to acid deposition. In 1991-92, soil samples were studied for sulphate adsorption. All the samples exhibited a tendency not to adsorb sulphate, at most added  $\text{SO}_4^{=}$  concentrations. The results of this study indicate that some soils in the province have very little neutralizing capacity for acids. Hence, any acidic deposition may cause metal-leaching from those soils. An Alberta Research Council (ARC) soil model also predicted that some of these soils may be acidified at the current acid loading rates.

A protocol document for sampling dry deposition and fine particulates with the combined annular denuder-filter pack (AD-FP) system was prepared. The document describes the preparation and field operation of the (AD-FP) system, as well as the analytical procedures for the determination of various parameters in the dry deposition.



A prototype dry deposition monitoring station was installed in November, 1991, at Royal Park (80 km east of Edmonton). The station is equipped with the AD-FP system to sample atmospheric pollutants on a six-day integrated basis and on randomly selected days. In addition, it has three wet deposition collectors (daily, weekly and monthly), a meteorological station, an ozone analyzer and a data logger to transfer data directly to an air information system at the Assessment Division. A Canadian Air Pollution Monitoring (CAPMON) filter pack system was installed in the summer of 1992. The objective of this project was to compare the AD-FP sampling system with the CAPMON system and recommend a suitable method to monitor the dry acidic deposition in the province. Although collection and analysis of the dry deposition samples started in November, 1991, this report contains data from that date to March, 1992. During this period, the mean concentrations of pollutants were:  $\text{SO}_2$ ,  $8.98 \mu\text{g}/\text{m}^3$  (as  $\text{SO}_4^{2-}$ );  $\text{HNO}_2$ ,  $0.22 \mu\text{g}/\text{m}^3$ ;  $\text{HNO}_3$ ,  $0.78 \mu\text{g}/\text{m}^3$ ; and  $\text{NH}_3$ ,  $1.71 \mu\text{g}/\text{m}^3$ . The  $\text{SO}_2$  value corresponds to 2.00 ppb in the atmosphere, and given a deposition velocity of  $0.7 \text{ cm S}^{-1}$ , to a dry deposition of 20 kg/ha/yr as  $\text{SO}_4^{2-}$ . These values are higher than those measured at Fortress Mountain, but comparable to those measured near Crossfield under the previous Acid Deposition Research Program (ADRP).

On February 20, 1992, the Acid Deposition Management Committee organized a workshop on "Effective Acidity". The purpose of the workshop was to examine the concept of "Effective Acidity" as a possible definition of "acidity", that will be useful under Alberta conditions. Several methods of calculating effective acidity based on Alberta data were also examined at the workshop. The general agreement at the workshop was that the "Effective Acidity" route is the reasonable route of choice to determine the target loading for Alberta.

### 1.3 Acid Deposition Inventory and Modelling

Under this project, an inventory of acid forming emissions was to be maintained and a computer data base established to keep the inventory data both current, and available for modelling purposes. The intent was to use the data for mass balance purposes, rather than surveillance of a particular industrial establishment for Alberta Clean Air Act compliance. In





## INTRODUCTION

The purpose of the Acid Deposition Program was to implement the "Acid Deposition Management Strategy for Alberta" approved by the Deputy Minister on March 21, 1989.

The goals of this program were:

1. To establish reliable methods for prediction of acid deposition within Alberta.
2. To provide scientific and technical knowledge for limiting acid deposition to protect sensitive forest, lake and soil systems in Alberta.
3. To monitor wet and dry deposition of acidic substances in sensitive areas of the province.

In order to achieve the above goals, the following areas of research were identified:

- Monitoring;
- Emissions Inventory and Modelling;
- Receptor Response;
- Technology Development.

## 1 OBJECTIVES

### 1.1 Monitoring

The objective of this project was to set up a network of air-chemistry observation stations equipped with wet and dry deposition monitoring equipment and state-of-the-art sensing and data acquisition systems. A data base was to be developed which could be populated with data from the observation network. Those data could be used for periodic public reports on the state of air-chemistry throughout the Province of Alberta, and for both simulation and predictive modelling. A prototype station was planned at Royal Park, near Vegreville.

### 1.2 Emissions Inventory and Modelling

Under this project, an inventory of acid forming emissions was to be maintained and a computer data base established to keep the inventory data both current, and available for modelling purposes. The intent was to use the data for mass balance purposes, rather than surveillance of a particular industrial establishment for Alberta Clean Air Act compliance. In



addition to emission data, the inventory data system was to contain information regarding source, deposition modelling, pollution control and compliance information, which could be used by the regulatory agencies. The objectives of the modelling project were to evaluate changes to emission sources, and effects of other environmental variables on the deposition of acid forming substances, as well as to establish a realistic and accurate mass balance for acid forming substances into and out of Alberta.

### 1.3 Receptor Response

The Acid Deposition Program was an operational program, consequently, research in this area was limited to key issues only, such as target loadings for water and soils. Under the receptor response project, the impact of acid deposition on sensitive soils and lakes was to be studied. Several recommendations related to forest, crop and health effects were also made in the ADRP final report, but work on those areas was dropped due to lack of funds.

### 1.4 Technology Development

Continuous monitors for measuring the atmospheric concentration of acidic and acid forming gases (dry deposition) in the vicinity of major sources of emissions are commercially available. However, these monitors generally lack sufficient sensitivity to measure concentrations at further distances from these sources.

Under this project, two objectives were considered. First, a three stage CAPMON (Canadian Air Pollution Monitoring) filter pack, and combined annular denuder with a two stage filter pack systems were to be used to collect gaseous and particulate acidic depositions. The two sampling systems needed to be examined and evaluated for their collection efficiencies and cost effectiveness in providing the information required for the monitoring and setting of target loading standards for Alberta. The second objective of this project was to determine the deposition velocity for the dry deposition.







## **SECTION 1**

**Preliminary Estimate  
of Sulphur Loadings  
in Alberta**





PRELIMINARY ESTIMATE  
OF SULPHUR LOADINGS  
IN ALBERTA

by

Lawrence Cheng

Environmental Research & Engineering Department  
Alberta Research Council

and

Randy P. Angle

Standards and Approvals Division  
Alberta Environment

for

ACID DEPOSITION PROGRAM  
ALBERTA ENVIRONMENT CENTRE

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## ABSTRACT

A preliminary estimate of sulphur loadings in Alberta has been generated using the RELMAP model. Annually, maximum ground level  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations in Alberta were located in the Edson area. The concentrations patterns possessed a northwest-southeast orientation, indicating the distributions of mean pollutant concentration are dictated by source regions and meteorology. The predicted maximum total sulphur deposition of  $4 \text{ kg ha}^{-1}$  was located in the Whitecourt-Hinton area. Maximum dry deposition occurred along the foothills west of Edmonton and maximum wet deposition was located near Whitecourt and Hinton. Annually, wet depositions were higher than dry depositions in Alberta, except close to emission sources and in drier regions. Monthly wet depositions were lowest in winter and highest in summer. On the other hand, dry deposition of  $\text{SO}_2$  contributed more to the seasonal sulphur loadings in Alberta than the other components in fall, winter and spring. The fraction of British Columbia emissions deposited in Alberta varied from 2% in the December to 42% in August. The percentage of Saskatchewan-Manitoba emissions that were deposited in Alberta was not significant, from negligible to 7%. Considerable variation existed in the amount of Alberta emissions deposited in Alberta, ranging from 2% in December to 74% in August. Because total emissions in Alberta were four times higher than those in British Columbia, over 70% of sulphur depositions in Alberta came from emission sources in Alberta. Emission sources in British Columbia contributed 7 to 28% of the monthly sulphur loading in Alberta, depending upon the meteorology of the month. Contributions from emission sources in Saskatchewan-Manitoba ranged from 0 to 15%.

## ACKNOWLEDGMENTS

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## 1. INTRODUCTION

Concern over acidic deposition and the development of control options has focussed attention on the need to understand the processes by which anthropogenic emission to the atmosphere cause acidification of terrestrial and aquatic ecosystems. Acidification results directly from the atmospheric deposition of acids and indirectly from the atmospheric deposition of acidifying substances which react in the ecosystems to form acids. The processes for transfer of acid and acid precursors from the atmosphere to the earth's surface are usually considered under two main headings: wet deposition in which pollutants are incorporated into cloud droplet (rainout) or scavenged by falling precipitation (washout) before being deposited as rain, snow or fog; and dry deposition in which gases (notably sulphur dioxide) or particles are directly collected by contact with land, water or biological surfaces.

Wet deposition consists of several steps: (1) intermixing of (gaseous or particulate) pollutants and the condensed phase of water in common airspace; (2) transfer and attachment of pollutants to condensed-water-elements (water droplet, ice crystal, raindrop and snow); (3) aqueous phase chemical reactions; and (4) deposition of pollutant-loaded precipitation on the ground.

Dry deposition includes all physical and chemical transformations that facilitate the removal of pollutants from the atmosphere to the earth's surface in the absence of water. The processes involved include: turbulent diffusion, Brownian motion (molecular diffusion), impaction, sedimentation, adsorption, absorption, and homogeneous and heterogeneous chemical reactions.

Long-term deposition of acidic and acid-forming substances can alter the structure and function of aquatic and terrestrial ecosystems. However, the prediction



of the impacts of acidic deposition on aquatic and terrestrial ecosystems is difficult because the effects are exceedingly complex, subtle and long-term. All ecosystems have an inherent capacity to resist acidification. A single standard on acidic loadings to preserve environmental integrity is not realistic. Thus, a reasonable management objective to protect sensitive ecosystems from acidic deposition is to balance acidic loadings with the sensitivity of a particular ecosystem to acidic deposition. The management strategy adopted in western and northern Canada has four basic elements: (1) determining the sensitivity of soil, geology and surface waters to acidic deposition, (2) establishing target loadings (objectives or ambient standards) that are suitable for the sensitivity of this environment, (3) monitoring to ensure compliance with the target loadings, and (4) establishing emission management plans as necessary. The critical loadings is the highest loading that will not cause chemical changes leading to long-term harmful effects on the most sensitive ecological systems. The target loading is less restrictive than critical loading, and takes into account other factors such as economical, social, or political considerations.

The last element of the strategy required that emissions from existing or planned industrial sources be linked with the ambient deposition rates. Acidic atmospheric deposition on the earth's surface can either be monitored or modelled. Historically, interest has been focussed on emissions of sulphur species and their deposition by wet route in sensitive environment, remote from their points of emission. Precipitation monitoring stations to measure the constituents and properties of wet deposition have been established in Alberta by both Alberta Environment and the Atmospheric Environment Service of Environment Canada. However, most of these stations are near urban centres or major point source emissions. The contribution of the dry deposition of sulphur in Alberta has only been estimated in the Acid Deposition Research Program (ADRP) from measured ambient gas concentrations and calculated deposition velocities (Legge and Krupa, 1990).

Mathematical modelling is the most cost-effective way of linking emissions to loading under complex meteorological and source conditions for regional scale. Modelling of the transport, chemical transformation and deposition of acidifying constituents is essential to interpolate or extrapolate monitoring data, because of the lack of sufficient monitoring data to define the level of loadings being experienced by the aquatic and terrestrial ecosystems. Moreover, atmospheric acid deposition modelling is the only method by which projection of effects due to future economic development can be made quantitatively.

Two mesoscale (20-2000km) atmospheric acid deposition models have been compared for their application in northern Alberta and Saskatchewan (Cheng et al., 1990). The MESOscale Puff (MESOPUFF-2) model is a short term (1 day to 1 month) acid deposition model. The REgional Lagrangian Model of Air Pollution (RELMAP) is a long term (1 month to 1 year) model.

MESOPUFF-2 (Scire et al., 1984) makes use of Briggs formulation to calculate plume rise. The boundary-layer structure is treated in terms of microphysical parameters that include the surface frictional velocity, mixing height, convective velocity scale, and Monin-Obhukov length. The model uses an integrated form of the puff sampling function that eliminates the problem of insufficient puff overlap commonly encountered with puff superposition models and provides concentrations and amounts of deposition at gridded and non-gridded (discrete) receptors. Therefore, MESOPUFF-2 has been considered the best overall Lagrangian mesoscale deposition model for short-term or episodic simulations (Thomson et al., 1987). The computational requirements of the model depend upon the simulation period, domain area, number of receptors, wind speed and direction, and number of emission sources. It is very costly for long-term simulations with numerous sources.

On the other hand, the pertinent physical and chemical processes in the RELMAP model (Eder et al., 1986) are highly parameterized by using available data and current theories to create a regional model capable of simulating monthly concentrations and depositions of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , and fine and coarse particulate matter. These parameterizations are representative for long-term periods (e.g., one month) and must not be interpreted as being representative for shorter periods. The model is designed as a regulatory tool and is operable with: (1) a small volume of input data, (2) short data processing and CPU times, and (3) low computer costs.

It has been shown that the two models produced similar results in regarding to monthly and seasonal wet and dry depositions of sulphur at stations downwind and/or in close vicinity of the emission source (Cheng et al., 1990). Furthermore, it has been concluded that RELMAP is more practical than MESOPUFF-2 for the calculation of monthly, seasonal and annual loadings. In a parallel effort, the U. S. National Acid Precipitation Assessment Program (NAPAP) has compared RELMAP with the more comprehensive state-of-the-art REGIONAL Acid Deposition Model, RADM, (NCAR, 1985) and shown that these models produced consistent annual wet and total sulphur deposition fields for eastern Northern America, though the peak dry deposition value predicted by RELMAP is almost twice that calculated by RADM (NAPAP, 1989). The discrepancy in maximum dry deposition value may be attributed to the Lagrangian setting in RELMAP and the Eulerian setting in RADM. An Eulerian model tends to diffuse more and produces smoother concentration fields.

RELMAP does not take into account any of the topographical effects on transport and deposition of acidic air pollutants. The topographical influences may be significant in simulating acidic loadings from a single point source in mountainous regions. For such applications as projection of impacts due to future economics development in complex terrain, modification to include an algorithm to account for the

complex airflow patterns over the mountainous area is required for RELMAP, or another suitable model should be chosen.

The objective of this study is to use the REgional Lagrangian Model of Air Pollution (RELMAP) to generate a preliminary estimate of sulphur loadings in Alberta to assist in selecting sites for regional deposition monitoring, to determine the contributions of transport from out-of-the-province sources to the sulphur depositions in Alberta and for data evaluation.

Following this brief introduction, an overview of the data base and the RELMAP model will be given in section 2. A preliminary estimate of sulphur loadings in Alberta will be presented in section 3. A brief discussion of the simulation results is given in section 4. Section 5 summarizes the findings and presents the recommendations.



## 2. DATA BASE AND THE RELMAP MODEL

### 2.1 DATA BASE

The model used in this study, like other numerical models, requires some input data and boundary conditions to initiate model simulations. In this section, the set of input data used will be discussed.

The area of interest in this study is the province of Alberta. Since pollutants can travel considerable distances and emissions from far-away sources can contribute significantly to the amounts of wet deposition, emission sources from neighbouring provinces were included. The north-south and east-west boundaries of the model domain were set from 47° to 62°N latitude and from 100° to 130°W longitude, respectively. Figure 1 gives the location of the study area.

The 1987 meteorological (surface and upper-air) data were obtained from the Canadian Climate Centre of the Atmospheric Environment Service, Environment Canada and the U. S. National Climate Data Center. Eight upper-air stations, five in the western Canada and three in Northwestern U. S., were used. These stations were: The Pas, Manitoba; Edmonton, Alberta; Fort Smith, Northwest Territories; Vernon and Port Hardy, British Columbia; Glasgow and Great Falls, Montana; and Spokane, Washington. The numbers of hourly surface meteorological and precipitation stations varied from hour to hour, depending upon the availability of data. On the average, 85 or more surface meteorological stations were used, up to the maximum of 94 at particular times. Precipitation was derived from 227 hourly stations within the study area. Figure 2 shows the locations of the precipitation stations.

Meteorological data were extracted from the magnetic tapes obtained from the

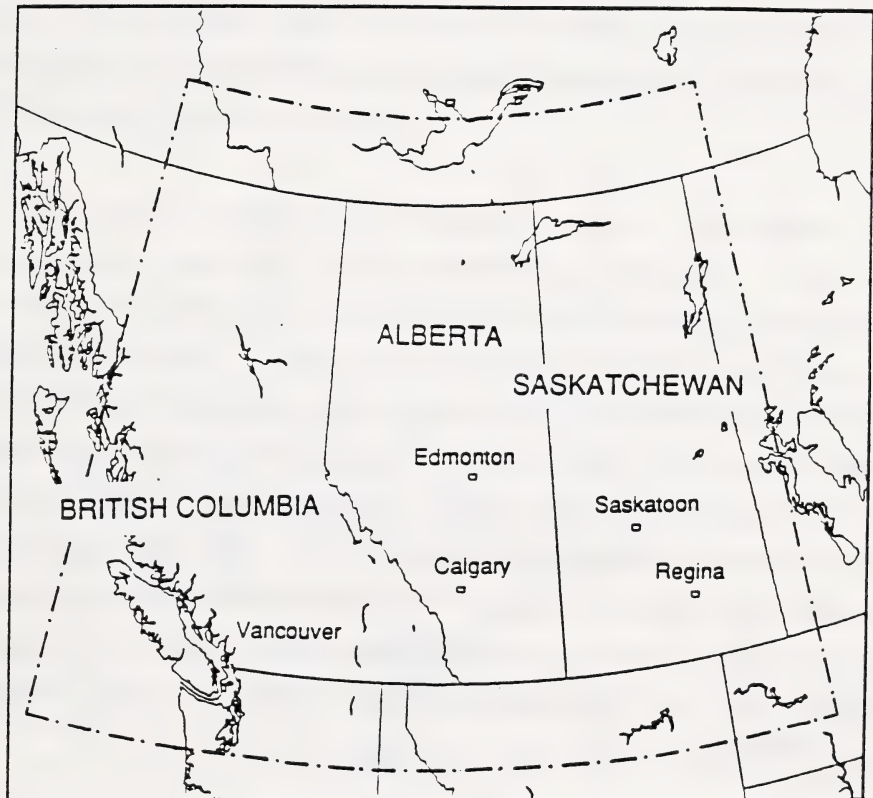


Figure 1.                      Location of the Study area.

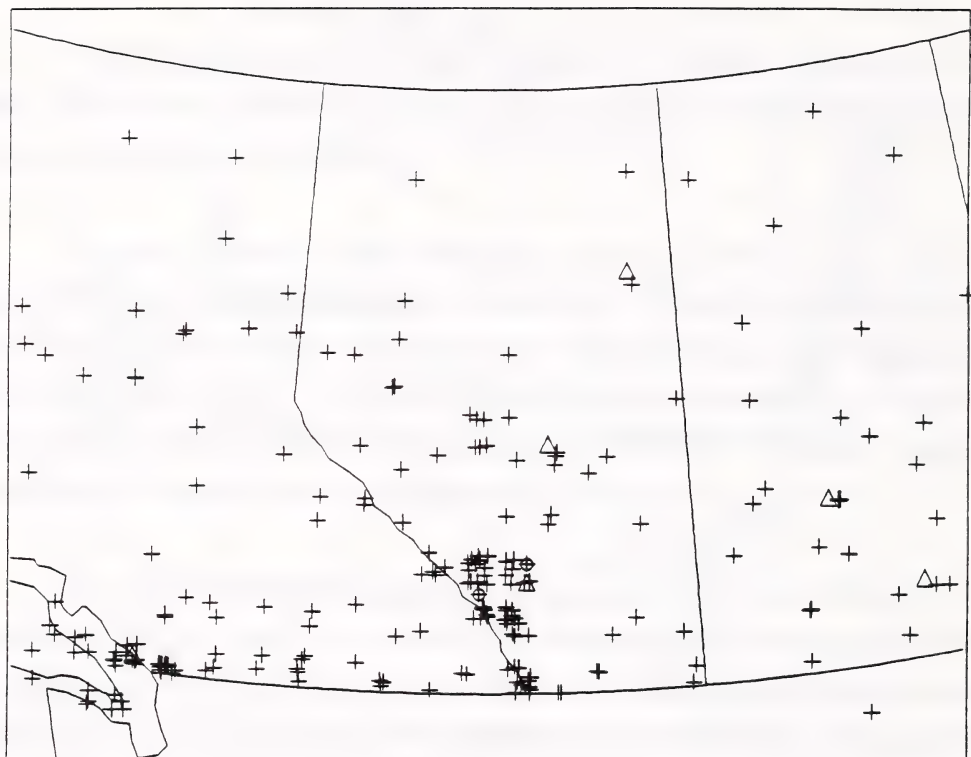


Figure 2. Locations of precipitation stations (+'s).  $\Delta$ 's denote the major cities and  $\oplus$ 's are the ADRP monitoring sites.

above-mentioned sources and were formatted into the National Center for Atmospheric Research (NCAR) data format which were used in the model. The processing of meteorological data is extremely time and storage demanding. To extract and convert a month's data required approximately 80 MB of disk space and 4.5 hours CPU on the VAX 6210 system.

Hourly surface observations of precipitation amount, wind direction, wind speed, temperature, dew point, and sky conditions were extracted. The u- and v-components of the surface wind, mixing height and stability category were calculated and gridded in two steps: (1) values are generated at every third grid cell in the north-south and east-west directions by using Barnes (1973) method; (2) with the  $1/R^2$  rule, intervening grid cells are evaluated by using the value of the grid cell closest to the intervening grid cell being evaluated. Figure 3 gives the gridded annual total precipitation amount for 1987. For later comparison purposes the locations of  $\text{SO}_2$  emission source are also plotted in the figure. The upper-air meteorological data were preprocessed by the model's preprocessors to produce gridded 12-h 850 mb winds, mixing heights and surface winds. These data were input files to the deposition model.

Emission inventory, based on 1984 production data, for  $\text{SO}_2$  sources in Alberta has been prepared by Picard et al. (1987) for the Alberta Government-industry Acid Deposition Research Program. The inventory includes 565  $\text{SO}_2$  sources with total emissions of  $1267 \text{ t d}^{-1}$ . This inventory was amalgamated, together with data for other provinces obtained from the Inventory Management Division of Environment Canada, into 49 sources for inputting to three statistical long range transport of air pollutant models (Leahey and Jamieson, 1987). Because a Lagrangian acid deposition model was used in this study, the computational demands were proportional to the number of emission sources. Hence, the amalgamated inventory of  $\text{SO}_2$  was employed to



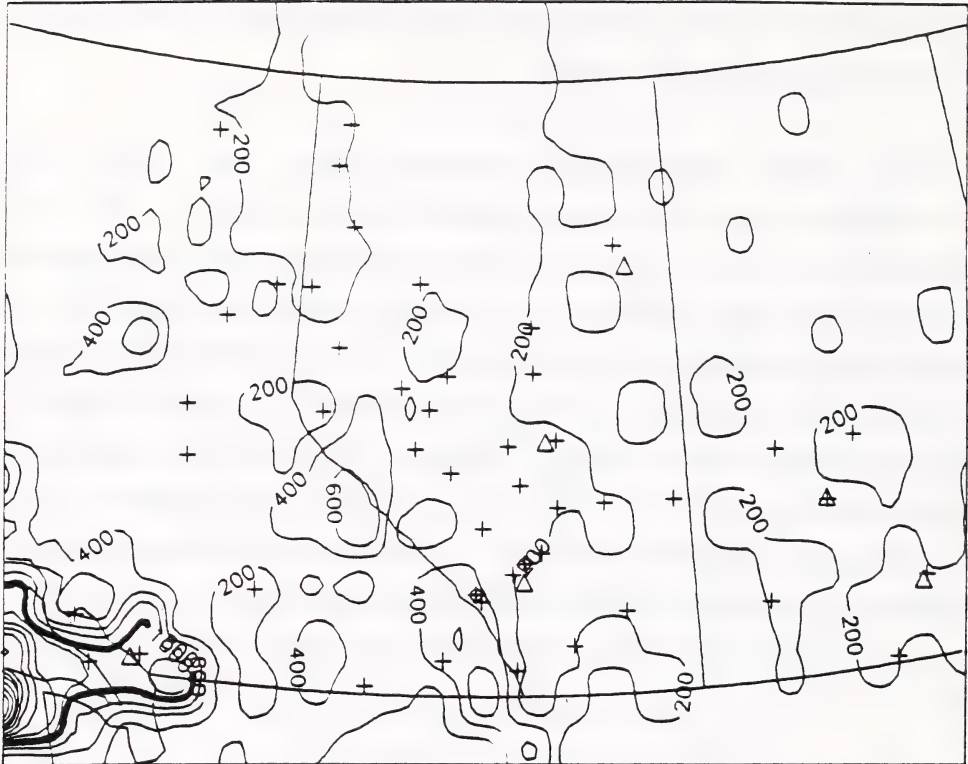


Figure 3. Total precipitation (mm) at western Canada for the year 1987. +'s denote locations of emission source and Δ's are major cities.

reduce the computer usage.

Because of the meteorology, it is believed that emissions from the U. S. sources do not contribute significantly to sulphur loadings in Alberta. The U. S. sulphur dioxide emissions were not considered in the calculation of preliminary sulphur loading estimates in this study. However, such an assumption needs to be proven in the future.

Table 1 lists the amalgamated sulphur dioxide sources used in this study. The location and emission rate are also given in the table and shown in Figure 4. Note that total emission from Alberta was higher than those from the other provinces, though the maximum single source (Flin Flon) was located in Manitoba, at the eastern edge of the model domain. Emissions from sources with stack heights greater than 100 m were injected into the middle layer (200-700 m) of the model. Other sources emissions were injected into the lowest layer.

Dry deposition of  $\text{SO}_2$  and sulphate is a highly variable, complex process that is parameterized in the deposition model used in this study as a function of predominant land use, stability index and season. Twelve land use categories, defined by surface characteristics and vegetation type were used in the deposition model. For Canada, the only available complete data bank for land use data consists of cells each  $10,000 \text{ km}^2$  (approximately  $1^\circ$  latitude  $\times$   $1^\circ$  longitude) in area. The land classification scheme specifies nine categories of forest, four of grassland, and seven for the remaining possibilities (fresh water, sea water, tundra, bog, rock, ice, and urban). The percentage frequency of occurrence of the land use types in each cell of the deposition model was interpolated from the original data and the surface characteristics and vegetation types were adjusted. The land use categories generated for the study area is given in Figure 5. The roughness length associated

TABLE 1  
AMMALGAMATED SULPHUR DIOXIDE EMISSION SOURCES  
IN WESTERN CANADA (kt/a)

Longitude	Latitude	Emission Rate	Source Area
BRITISH COLUMBIA SOURCES			
130.28	54.23	0.8	Prince Rupert
128.71	54.00	6.9	Kitamat
126.87	50.24	4.5(0.9)	Kyuquot, Campbell River
124.57	49.87	0.9(0.9)	Westwiew
124.07	49.07	2.4	Port Alberni, Crofton, Duncan
122.97	49.33	6.5(0.4)	Vancouver
122.78	58.84	20.6	Ft. Nelson
122.78	53.90	3.8	Prince George
122.50	53.00	1.1	Quesnel
121.93	55.57	21.8	Chetwynd
120.68	56.21	22.0	Ft. St. John
120.49	50.73	10.9(8.5)	Copper Creek
117.75	49.14	22.2(6.2)	Trail, Castlegar
115.97	49.63	4.4	Kimberly, Shookumchuck
		TOTAL	128.8
ALBERTA SOURCES:			
119.73	56.22	0.6	Boundary Lake., Braeburn, Spirit River
119.23	58.43	3.8	Rainbow Area
119.18	54.00	5.8(5.8)	Grande Cashe
118.98	59.17	3.4	Zama, Shekille, Virgo Areas
118.87	55.15	2.6	Grande Prairie, Gold Creek, Hythe
117.17	54.48	17.8(17.8)	Bigstone, Kaybob
116.78	56.37	3.3	Pease River Area
116.77	53.42	12.3	Hinton, Roseveau, Galloway, Edson
116.44	54.12	32.6(12.4)	Whitcourt, Kaybob, Carson Creek
116.00	54.72	1.3	Swan Hills Area
115.87	53.00	7.3(4.2)	Brazeau, W. Pembina
115.08	50.70	0.1	Empress
115.06	52.01	63.7	Caroline, Innisfail, Olds, Sundre
114.43	53.48	56.0(33.9)	Wabamun, Keephills Area
114.33	51.19	40.8	Calgary, Okotoks, Morley
114.24	49.46	14.8	Pincher Creek, Coleman, Waterton
114.15	52.78	6.6	Gilby, Rimbey, Minnehik
113.80	55.60	0.1	Marten Hills
113.77	54.77	0.2	Athabasca, Baptiste Lake, Big Bend
113.65	51.57	12.7(12.7)	Drumheller, Winborne, Balzac

Continued.....

TABLE 1 CONCLUDED  
AMALGAMATED SULPHUR DIOXIDE EMISSION SOURCES  
IN WESTERN CANADA (kt/a)

Longitude	Latitude	Emission Rate	Source Area
ALBERTA SOURCES: (continued)			
113.23	52.37	7.8	Nevis, Bashaw, Chigwell, Joffre
113.23	53.58	13.8	Edmonton, Ft. Saskatchewan Areas
112.92	49.88	1.9	Vulcan, Retlaw, Long Coulee
112.08	52.43	24.0	Duhamel, Sedgewick, Killam Areas
112.52	57.02	129.6(129.6)	Ft. McMurray
110.37	52.43	0.3	David
	TOTAL	463.0	
SASKATCHEWAN AND MANITOBA SOURCES:			
108.28	50.43	0.1	Success
107.77	53.13	0.5	Rabbit Lake
106.63	52.12	0.9	Saskatoon
105.52	49.12	39.3	Borderland, Coronach
105.77	53.20	0.4	Prince Albert
104.55	50.50	16.8	Regina, Moose Jaw
102.93	49.16	36.0	Estevan, Steelman, Weyburn
101.88	54.77	248.3	Flin Flon
101.25	53.88	1.2	The Pas
	TOTAL	343.5	

Sulphur dioxide emissions from sources with stack heights greater than 100 m are given in parenthesis.



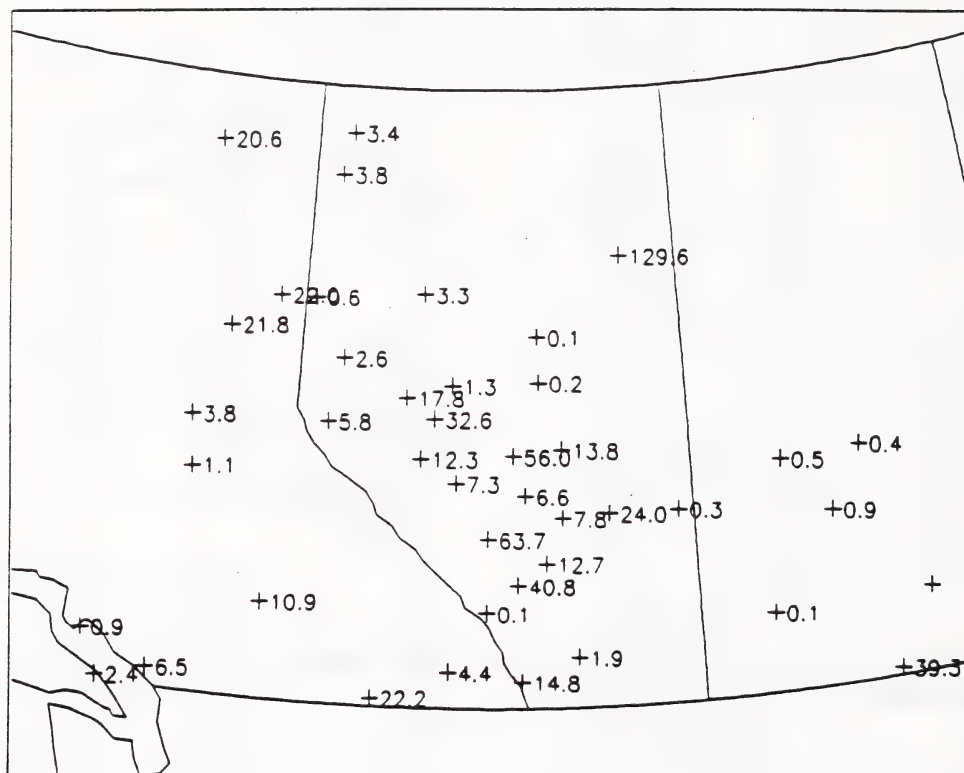
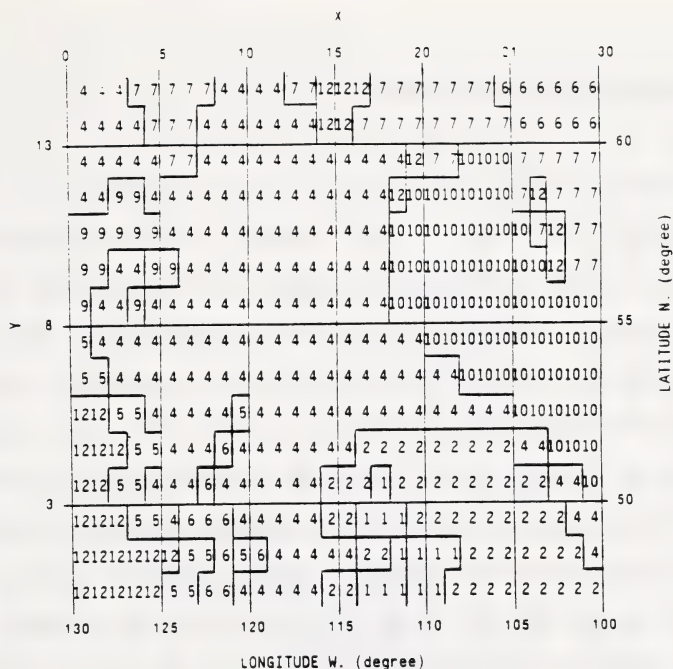


Figure 4. Spatial distribution of SO<sub>2</sub> emissions (kt/a).



Symbol	Land Use Type	$Z_0$ (cm)
1	Cropland and Pasture	20
2	Cropland, Woodland, and Grazing	30
3	Irrigated Crops	5
4	Grazed Forest and Woodland	90
5	Ungrazed Forest and Woodland	100
6	Subhumid Grassland and Semiarid Grazing	10
7	Open Woodland, Grazed	20
8	Desert Shrubland	30
9	Swamp	20
10	Marshland	50
11	Metropolitan City	100
12	Lake or Ocean	0.01

Figure 5. Land use categories used for dry deposition calculations and corresponding surface roughness length  $z_0$ .

with each land use category is also presented.

The atmospheric stability used to determine the dry deposition velocities are the six Pasquill-Gifford categories: (A) very unstable, (B) moderately unstable, (C) slightly unstable, (D) neutral, (E) moderately stable, and (F) very stable. Tables 2 and 3 give the dry deposition velocities for  $\text{SO}_2$  and sulphate for the various stability, season, and land use categories. The calculation of dry deposition velocities were based on the algorithm suggested by Sheih et al. (1979). For  $\text{SO}_4^{2-}$ , the calculated dry deposition velocities had been reduced by half, since more recent studies (Wesely and Shannon, 1984) concluded that earlier dry deposition velocities of  $\text{SO}_4^{2-}$  were too high by a factor of two. Use of the deposition velocity tables for stability categories A through F is not always accurate when considering diurnal variations. In nearly calm conditions at night, atmospheric resistances become very large for both gaseous and particulate sulphur deposition, and such conditions are not adequately represented by Pasquill stability category F. To compensate for the very high nocturnal atmospheric resistance, when plant absorption is minimal, the dry deposition velocities for  $\text{SO}_2$  and sulphate are reduced to  $0.07 \text{ cm s}^{-1}$  during the nighttime hours (Sheih et al., 1979).

## 2.2 MODEL DESCRIPTION

RELMAP consists of 19 pre-processing programs that prepare gridded meteorological and emission data for use in the main program. The model is a mass-conserving, regional-scale Lagrangian model and performs monthly (default) simulations on a user-defined latitude-longitude grid with a user-defined degree of resolution. In this study, the north-south and east-west boundaries of the model's domain extend from  $47^\circ$  to  $62^\circ\text{N}$  latitude and from  $100^\circ$  to  $130^\circ\text{W}$  longitude, respectively. The grid intervals are  $1^\circ$  in latitude and longitude.

Table 2. Seasonal SO<sub>2</sub> dry deposition velocities (cm s<sup>-1</sup>) by land use category and P-G stability class.

Land Use Category	Winter						Spring					
	A	B	C	D	E	F	A	B	C	D	E	F
Cropland and Pasture	0.30	0.35	0.35	0.15	0.05	0.25	0.65	0.75	0.75	0.35	0.05	0.55
Cropland, Woodland and Grazing Land	0.30	0.35	0.35	0.15	0.05	0.30	0.65	0.75	0.75	0.35	0.05	0.65
Irrigated Crops	0.20	0.25	0.40	0.15	0.05	0.30	0.45	0.55	0.85	0.35	0.05	0.45
Grazed Forest and Woodland	0.40	0.40	0.40	0.15	0.05	0.40	0.85	0.85	0.85	0.35	0.05	0.85
Ungrazed Forest and Woodland	0.40	0.40	0.40	0.15	0.05	0.40	0.85	0.85	0.85	0.35	0.05	0.85
Semihumid Grassland and Semiarid Grazing Land	0.25	0.30	0.35	0.10	0.05	0.20	0.55	0.65	0.75	0.25	0.05	0.45
Open Woodland, Grazed	0.30	0.35	0.35	0.10	0.05	0.25	0.65	0.75	0.75	0.25	0.05	0.55
Desert Shrubland	0.20	0.20	0.40	0.15	0.05	0.05	0.45	0.45	0.85	0.35	0.05	0.05
Swamp	0.45	0.55	0.35	0.45	0.25	0.25	0.95	1.15	0.75	0.95	0.55	0.55
Marshland	0.45	0.50	0.40	0.15	0.05	0.35	0.95	1.05	0.85	0.35	0.05	0.75
Metropolitan City	0.05	0.05	0.05	0.05	0.05	0.40	0.05	0.05	0.05	0.05	0.05	0.85
Lake or Ocean	0.10	0.15	0.25	0.35	0.15	0.10	0.25	0.35	0.55	0.75	0.35	0.15

Continued .....



Table 2. Concluded.

Land Use Category	Summer						Autumn					
	A	B	C	D	E	F	A	B	C	D	E	F
Cropland and Pasture	0.65	0.75	0.75	0.35	0.05	0.55	0.50	0.55	0.55	0.25	0.05	0.40
Cropland, Woodland and Grazing Land	0.65	0.75	0.75	0.35	0.05	0.65	0.50	0.55	0.55	0.25	0.05	0.50
Irrigated Crops	0.45	0.55	0.85	0.35	0.05	0.45	0.35	0.40	0.65	0.25	0.05	0.35
Grazed Forest and Woodland	0.85	0.85	0.85	0.35	0.05	0.85	0.65	0.65	0.65	0.25	0.05	0.65
Ungrazed Forest and Woodland	0.85	0.85	0.85	0.35	0.05	0.85	0.65	0.65	0.65	0.25	0.05	0.65
Semihumid Grassland and Semiarid Grazing Land	0.55	0.65	0.75	0.25	0.05	0.45	0.40	0.50	0.55	0.20	0.05	0.35
Open Woodland, Grazed	0.65	0.75	0.75	0.25	0.05	0.55	0.50	0.55	0.55	0.20	0.05	0.40
Desert Shrubland	0.45	0.45	0.85	0.35	0.05	0.05	0.35	0.35	0.65	0.25	0.05	0.05
Swamp	0.95	1.15	0.75	0.95	0.55	0.55	0.70	0.85	0.55	0.70	0.40	0.40
Marshland	0.95	1.05	0.85	0.35	0.05	0.75	0.70	0.80	0.65	0.25	0.05	0.55
Metropolitan City	0.05	0.05	0.05	0.05	0.05	0.85	0.05	0.05	0.05	0.05	0.05	0.65
Lake or Ocean	0.25	0.35	0.55	0.75	0.35	0.15	0.20	0.25	0.40	0.55	0.25	0.10

Table 3. Seasonal  $SO_4^{2-}$  dry deposition velocities ( $cm\ s^{-1}$ ) by land use category and P-G stability class.

Land Use Category	Winter						Spring					
	A	B	C	D	E	F	A	B	C	D	E	F
Cropland and Pasture	0.20	0.20	0.20	0.20	0.20	0.10	0.30	0.35	0.35	0.35	0.25	0.15
Cropland, Woodland and Grazing Land	0.20	0.20	0.20	0.20	0.20	0.10	0.35	0.35	0.35	0.35	0.30	0.15
Irrigated Crops	0.15	0.20	0.20	0.20	0.15	0.10	0.25	0.30	0.30	0.30	0.20	0.15
Grazed Forest and Woodland	0.25	0.25	0.25	0.25	0.20	0.15	0.40	0.40	0.40	0.40	0.35	0.20
Ungrazed Forest and Woodland	0.25	0.25	0.25	0.25	0.20	0.15	0.40	0.40	0.40	0.40	0.35	0.20
Semihumid Grassland and Semiarid Grazing Land	0.20	0.20	0.20	0.20	0.15	0.10	0.30	0.30	0.35	0.35	0.25	0.15
Open Woodland, Grazed	0.20	0.20	0.20	0.20	0.15	0.10	0.30	0.35	0.35	0.35	0.25	0.15
Desert Shrubland	0.20	0.20	0.20	0.20	0.20	0.10	0.35	0.35	0.35	0.35	0.30	0.15
Swamp	0.20	0.20	0.20	0.20	0.20	0.10	0.30	0.35	0.35	0.35	0.25	0.15
Marshland	0.25	0.25	0.25	0.25	0.20	0.15	0.40	0.40	0.40	0.40	0.30	0.20
Metropolitan City	0.25	0.25	0.25	0.25	0.20	0.15	0.40	0.40	0.40	0.40	0.35	0.20
Lake or Ocean	0.05	0.05	0.10	0.10	0.05	0.05	0.10	0.10	0.15	0.15	0.10	0.10

Continued.....

Table 3. Concluded.

Land Use Category	Summer						Autumn					
	A	B	C	D	E	F	A	B	C	D	E	F
Cropland and Pasture	0.40	0.45	0.45	0.45	0.45	0.35	0.20	0.30	0.35	0.35	0.25	0.15
Cropland, Woodland and Grazing Land	0.45	0.45	0.45	0.45	0.40	0.20		0.35	0.35	0.35	0.30	0.15
Irrigated Crops	0.35	0.40	0.40	0.40	0.30	0.20		0.25	0.30	0.30	0.20	0.15
Grazed Forest and Woodland	0.50	0.50	0.50	0.50	0.45	0.30		0.40	0.40	0.40	0.35	0.20
Ungrazed Forest and Woodland	0.50	0.50	0.50	0.50	0.45	0.30		0.40	0.40	0.40	0.35	0.20
Semihumid Grassland and Semiarid Grazing Land	0.40	0.40	0.45	0.45	0.35	0.20		0.30	0.30	0.35	0.25	0.15
Open Woodland, Grazed	0.40	0.45	0.45	0.45	0.35	0.20		0.30	0.35	0.35	0.25	0.15
Desert Shrubland	0.45	0.45	0.45	0.45	0.40	0.20		0.35	0.35	0.35	0.30	0.15
Swamp	0.40	0.45	0.45	0.45	0.35	0.20		0.30	0.35	0.35	0.25	0.15
Marshland	0.50	0.50	0.50	0.50	0.40	0.30		0.40	0.40	0.40	0.30	0.20
Metropolitan City	0.50	0.50	0.50	0.50	0.45	0.30		0.40	0.40	0.40	0.35	0.20
Lake or Ocean	0.10	0.10	0.20	0.20	0.10	0.10		0.10	0.10	0.15	0.10	0.10

RELMAP divides the atmospheric boundary layer into three layers, into which emissions are injected. The first layer is between the surface and 200 m, and the second layer is between 200 to 700 m. The depth of the third layer depends upon the maximum mixing height. Discrete puffs of  $\text{SO}_2$  are released every 12 h. The mass of the pollutant emitted is determined by the monthly emissions. Emissions from point sources with stack height greater than 100 m are allocated into layer two, accounting for typical plume rise.

RELMAP parameterizes both horizontal and vertical diffusion very simply. During the unstable regimes of midday periods, pollutants became well mixed below the mixing height well before the pollutants are transported a distance comparable to the spatial resolution of the grid. Instantaneous, complete mixing within the three layers of the model is assumed. After sunset, when mixing is precluded by stable conditions, emissions are confined to the layer of injection. Horizontal diffusion of the puffs in the model occurs at a constant rate, so that the area of each puff increases at a rate of  $339 \text{ km}^2 \text{ h}^{-1}$  (Clarke, et al., 1983). Pollutant mass in the puff is homogeneous in the horizontal plane at all time.

Each puff is transported in 2 h (default) time steps by using vertically integrated and horizontally and temporally interpolated wind fields until the puff is either transport out of the model's domain or the mass of the pollutant falls below user-defined minimum values. Vertical shear is not directly considered as a component of the transport process, thus avoiding the significant increase in computer time required to track branching puff segments. However, its effect is considered inherently in the enhanced horizontal diffusion rate of the puff. The transport velocity of the puffs is determined by integrating mass-weighted u- and v-components of the three layers, which are derived from the preprocessed wind velocities for the grid cell



containing the puff's centroid. Wind velocity in the top layer is the 850 mb wind velocity, and the wind velocity in the middle layer is a weighted average of surface (weighted 0.2) and 850 mb (weighted 0.8) wind velocities.

Any parameterization used to simulate the complex chemical processes within the atmospheric boundary layer is only accurate to a limited degree. Chemical transformation rates used in all air quality models are based on laboratory experiments and a limited number of field studies. Therefore, discrepancies with real-world transformation rates may occur. Linear chemical transformation processes are simulated as the puff is transported across the model's domain in RELMAP. For each time step, the suspended pollutant mass of each puff is apportioned into the appropriate grid cells based on the percentage of puff over each grid cell.

RELMAP considered the effects of solar insolation and moisture content on the transformation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ , either explicitly or implicitly. The transformation rate consists of two components: one for dry conditions (homogeneous component), and one for saturated conditions (heterogeneous component). A minimum transformation rate of  $0.02\% \text{ h}^{-1}$  is defined, regardless of time or season as estimated by Meagher et al. (1978). The homogeneous component is a function of latitude, length of the day, and hour of the day. The heterogeneous component of the transformation rate accounts for the more rapid in-cloud transformation process. Based on the study of Scott (1982), the heterogeneous component of conversion is defined as  $7\% \text{ h}^{-1}$  for winter,  $11\% \text{ h}^{-1}$  for spring and autumn, and  $15\% \text{ h}^{-1}$  for summer to account for the seasonal variations.

The complex process of wet deposition of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  is parameterized in RELMAP as a function of season and precipitation rate. The wet deposition rates are expressed as percentages per time step and are based on the work of Scott (1978).

It was assumed that all winter precipitation results from the Bergeron process, that spring and fall precipitation result from layered synoptic scale storm where the development of rain is independent of the Bergeron process, and the summer precipitation is confined to intense convective-type storms or storms whose cloud tops are warmer than 0°C. The wet deposition rate is calculated by:

$$\text{Wet Deposition Rate} = 1.0 - (1.0 - aR^b)^t \quad (1)$$

where a and b are seasonal empirical constants derived from the inherent relationship between the washout ratio and the mean precipitation rate (R) in mm h<sup>-1</sup>. The parameter t is the time step, in hours, selected by the users. Table 4 gives the seasonal empirical constants for SO<sub>2</sub> and sulphate wet deposition rate calculations. Hence, SO<sub>2</sub> wet deposition rates for a constant precipitation rate of 5 mm h<sup>-1</sup> for a 2-h simulation time step range from 0.0548 to 0.3108 (2 h)<sup>-1</sup> and SO<sub>4</sub><sup>2-</sup> wet deposition

TABLE 4  
DEFAULT SEASONAL EMPIRICAL CONSTANTS FOR  
SO<sub>2</sub> AND SO<sub>4</sub><sup>2-</sup> WET DEPOSITION RATE CALCULATION

Pollutant	Season	Empirical Constants	
		a	b
SO <sub>2</sub>	Summer	0.140	0.12
	Fall/Spring	0.036	0.53
	Winter	0.009	0.70
SO <sub>4</sub> <sup>2-</sup>	Summer	0.390	0.06
	Fall/Spring	0.091	0.27
	Winter	0.021	0.70

rates range from 0.1254 to 0.6746 (2 h)<sup>-1</sup>, depending upon the season.

It has been shown that RELMAP strongly over-predicts wet deposition in summer (Eder et al., 1986). Furthermore, all precipitating clouds in Alberta have top colder than 0°C, and precipitation development in Alberta summer cumulus clouds or convective storms is believed to be dominated by the Bergeron or ice growth process (English and Marwitz, 1981; Krauss and Marwitz, 1984). This means that the default summer constants for wet deposition will overestimate the wetfall of sulphur. Thus, this study assumes that all winter precipitation results from the Bergeron process, and that spring, autumn and summer precipitation results from layered synoptic scale storms. This simplistic approach to the wet removal processes may overestimate the spring and fall wet deposition and underestimate the summer wet deposition in Alberta somewhat. However, summer convective storms in Alberta produce heavy precipitation rates and it has been demonstrated that the washout ratio is virtually independent of the mechanisms of precipitation formation (Scott, 1978) at heavy precipitation rates. Nevertheless, the values of wet deposition rate constants,  $a$  and  $b$ , can be replaced in the future with more sophisticated parameterizations or more reliable values once they are determined or available.

### 3. SIMULATION RESULTS

#### 3.1 LOADING ESTIMATES

Monthly simulations were performed using RELMAP to simulate monthly averaged ground level concentrations, and monthly wet and dry depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ . Seasonal and annual averaged concentrations and the amounts of dry, wet and total depositions for the respective periods were generated from the monthly values. The seasonal simulation results are presented in Appendix for the interested readers.

Simulated annual averaged  $\text{SO}_2$  concentration at ground level is shown in Figure 6. Locations of the emission sources are also shown with crosses. Typical values for Alberta ranged from  $<0.1 \text{ } \mu\text{g m}^{-3}$  in the extreme north to  $2.0 \text{ } \mu\text{g m}^{-3}$  at the foothill west of Edmonton. The maximum annual concentration within the model's domain was at Flin Flon, associating with the largest emission source considered. Aside from the Edson area, maximum annual concentration of  $1.4 \text{ } \mu\text{g m}^{-3}$  was located near the oil sands plants at Fort McMurray. The distribution of the concentrations is seen to be determined primarily by the location of  $\text{SO}_2$  sources, with some effect of prevailing meteorology evident in the northwest-southeast orientation of the contours.

Annual averaged sulphate concentration is shown in Figure 7. Because dispersion and transport of  $\text{SO}_2$  must take place during the production of sulphate, the sulphate distribution is very similar to that of the sulphur dioxide concentration. Maximum annual concentration of sulphate of  $0.4 \text{ } \mu\text{g m}^{-3}$  occurred downwind (east and southeast) from the  $\text{SO}_2$  concentration maximum at the Edson area, as well as of  $0.2 \text{ } \mu\text{g m}^{-3}$  at Fort McMurray.



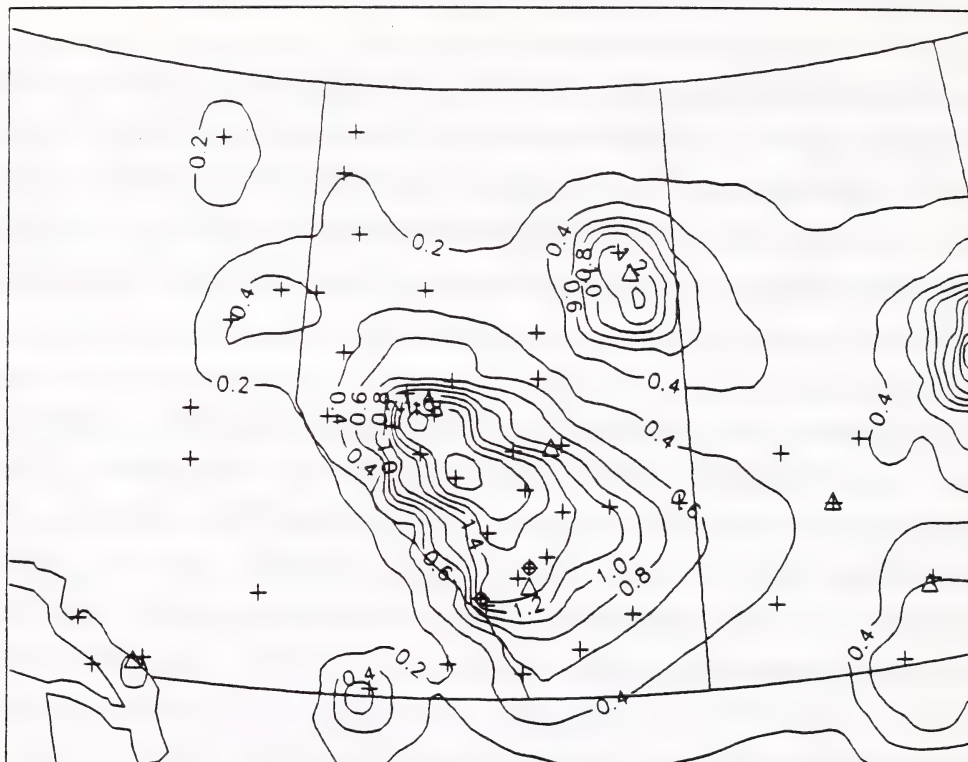


Figure 6. Predicted annual average SO<sub>2</sub> concentration ( $\mu\text{g m}^{-3}$ ). +'s denote locations of emission source and \Delta's are major cities.

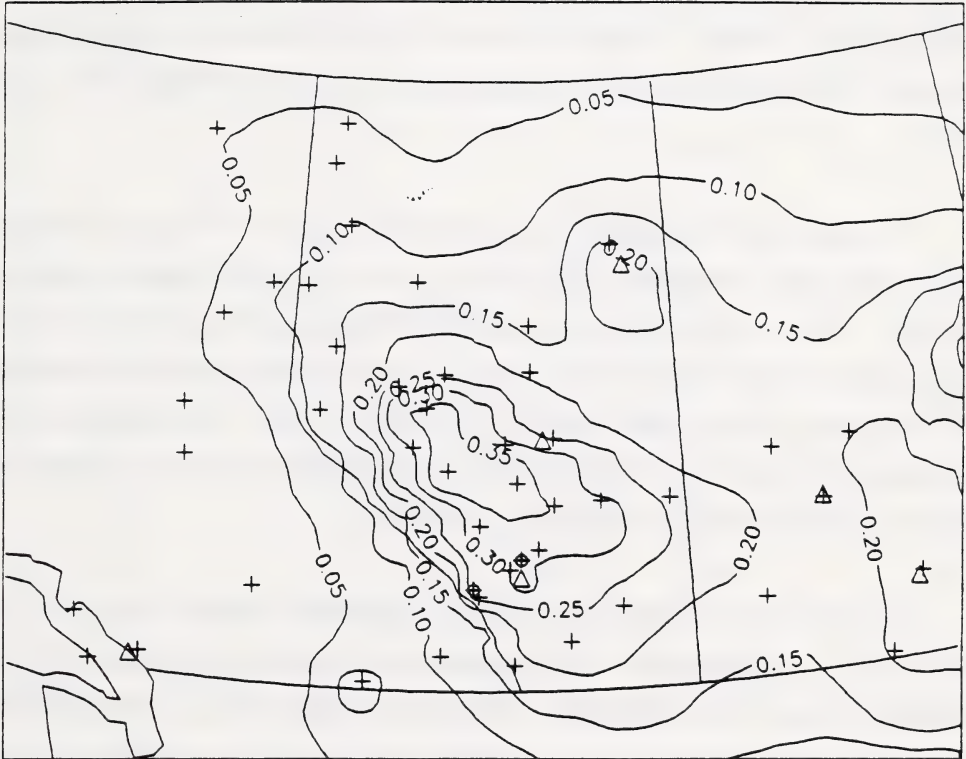


Figure 7. Predicted annual average  $\text{SO}_4^{2-}$  concentration ( $\mu\text{g m}^{-3}$ ). '+'s denote locations of emission source and '\Delta's are major cities.

The results indicated that patterns of mean pollutant concentration across Alberta are dictated by source regions and meteorology. Furthermore, it showed that the densely located smaller sources in central Alberta combine to produce the highest concentrations in Alberta. Average pollutant concentrations were relatively low in comparison with populated and industrialized areas of eastern Canada and the United States.

The distribution of annual  $\text{SO}_2$  dry deposition is given in Figure 8. Similar to sulphate production, dispersion and transport of  $\text{SO}_2$  must take place for  $\text{SO}_2$  dry deposition. Thus, the annual  $\text{SO}_2$  dry deposition distribution is very similar to that of the  $\text{SO}_2$  concentration. Maximum dry depositions of  $\text{SO}_2$  were located downwind from major emission sources, with values of  $1.6 \text{ kg ha}^{-1}$  along the foothills west of Edmonton and  $1.1 \text{ kg ha}^{-1}$  at Fort McMurray. The extreme north of the province, the dry deposition of  $\text{SO}_2$  was very low, about  $0.1 \text{ kg ha}^{-1}$ .

The distribution of annual dry deposition of sulphate is shown in Figure 9. The pattern of the predicted sulphate dry deposition was smoother than that of  $\text{SO}_2$  and the concentrations of  $\text{SO}_2$  and sulphate, most likely because of its lower dry deposition velocity. The maximum sulphate dry deposition of  $0.3 \text{ kg ha}^{-1}$  was located at central Alberta, extending from the foothills to the Alberta-Saskatchewan border and between Edmonton and Calgary. The annual dry deposition of sulphate was, in general, one-third to one-fifth that of  $\text{SO}_2$  at any location within the province.

Annual wet depositions of  $\text{SO}_2$  and sulphate are presented in Figures 10 and 11. Unlike the distributions of concentrations and dry depositions which have been shown earlier, the distributions of wet depositions, both of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , were very patchy. Precipitation in the prairies is mainly from convective type of storms and, therefore, very isolated. The large number of precipitation stations used in this study

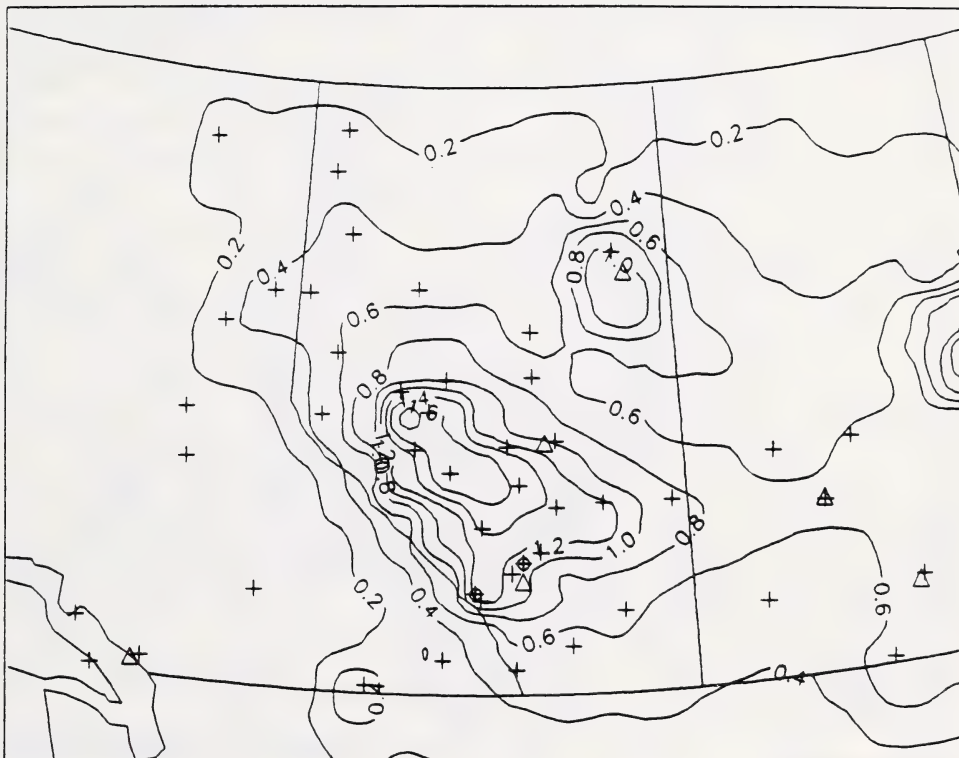


Figure 8. Predicted annual SO<sub>2</sub> dry deposition (kg ha<sup>-1</sup>). +'s denote locations of emission source and Δ's are major cities.



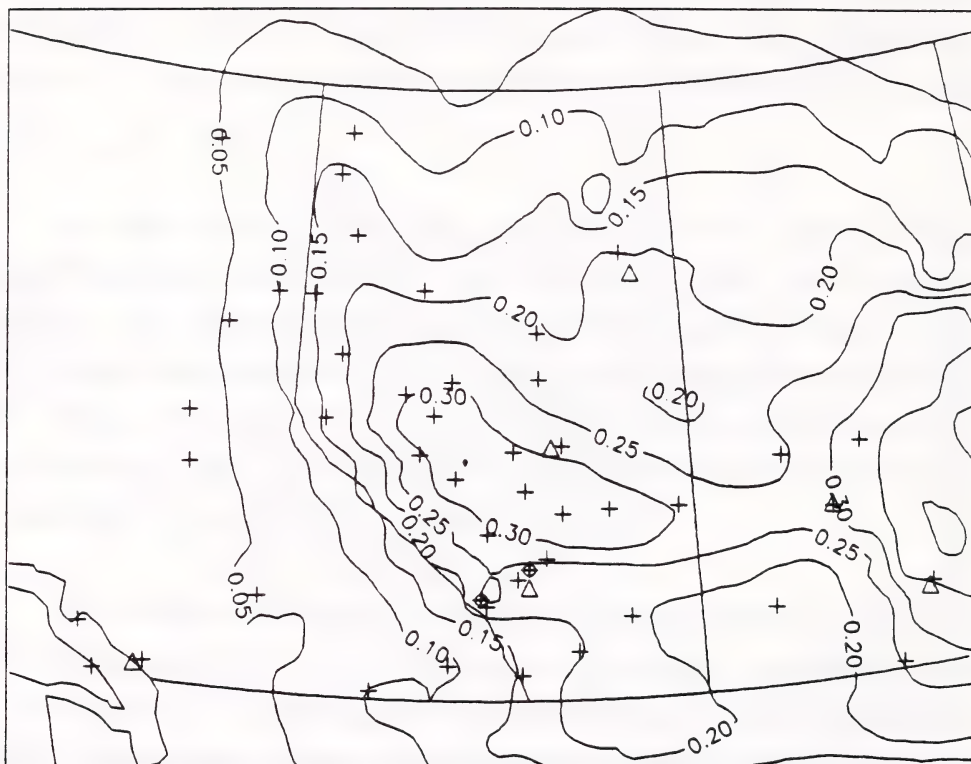


Figure 9. Predicted annual  $\text{SO}_4^{2-}$  dry deposition ( $\text{kg ha}^{-1}$ ). '+'s denote locations of emission source and '\Delta's are major cities.

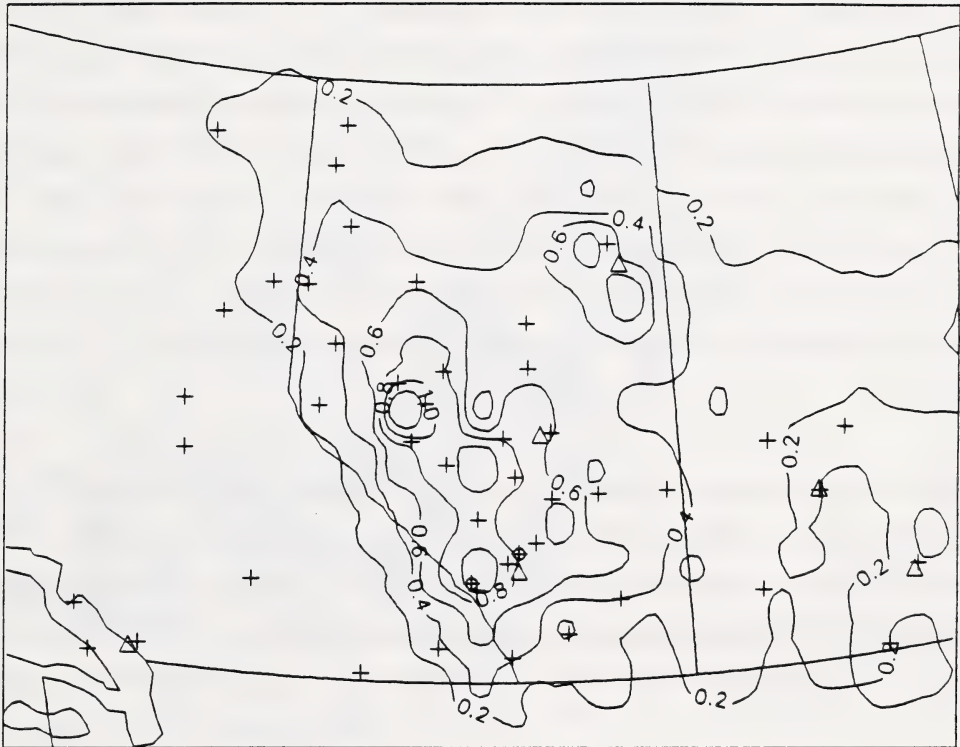


Figure 10. Predicted annual SO<sub>2</sub> wet deposition (kg ha<sup>-1</sup>). +'s denote locations of emission source and Δ's are major cities.

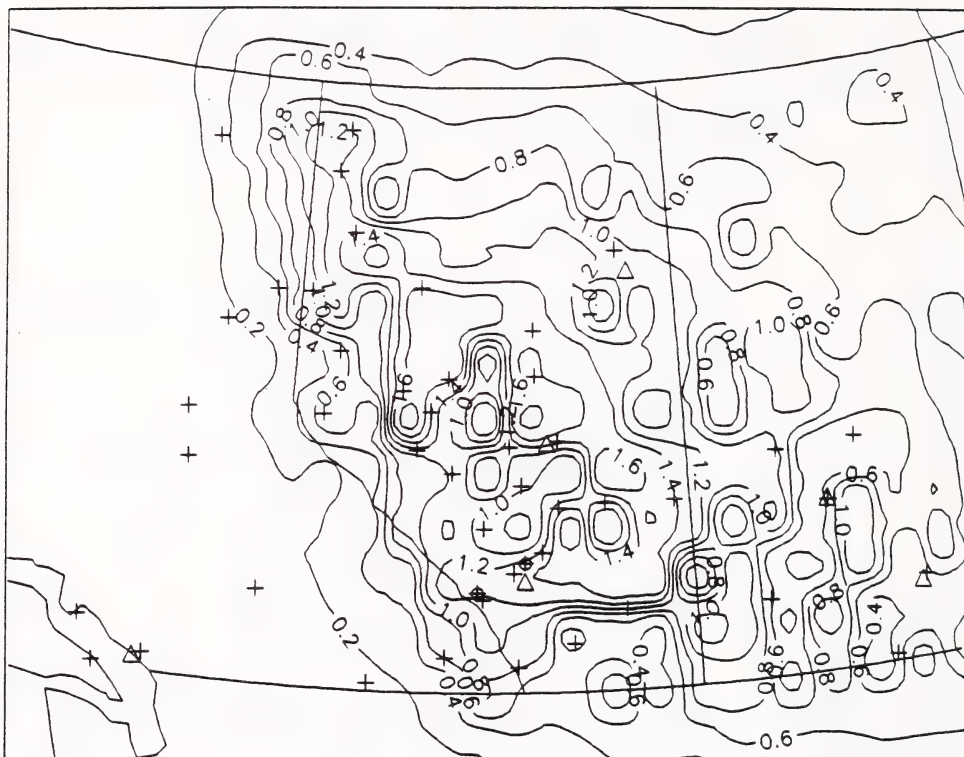


Figure 11. Predicted annual  $\text{SO}_4^{2-}$  wet deposition ( $\text{kg ha}^{-1}$ ). reflects the scattered nature of precipitation events in the wet deposition patterns.

reflects the scattered nature of precipitation events in the wet deposition patterns. Reducing the number of precipitation stations would make the distributions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  wet depositions smoother. Maximum annual  $\text{SO}_2$  wet deposition of  $1.2 \text{ kg ha}^{-1}$  in Alberta was located in the Whitecourt and Hinton region. Aside from the Whitecourt-Hinton area, maximum annual  $\text{SO}_2$  wet depositions of  $0.8 \text{ kg ha}^{-1}$  were near Fort McMurray and Edson. The amount of wet deposition of sulphate in Alberta was larger than that of sulphur dioxide, and the locations of were almost identical. The maximum annual sulphate wet depositions of 1.8, 1.2 and 1.8 were near Whitecourt-Hinton, Fort McMurray and Edson areas respectively. The minimum wet depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  were at the extreme north and extreme south of the province. The minimum wet depositions in southern Alberta is the result of dryness in that area.

Since  $\text{SO}_2$  in water rapidly oxidize to  $\text{SO}_4^{2-}$ , the total wet deposition of sulphur will be closer to the quantity measured by monitoring stations. The annual wet deposition of sulphur is shown in Figure 12. The distribution was very similar to those of the individual components. Maximum wet depositions of sulphur near Whitecourt-Hinton, Fort McMurray and Edson areas were  $1.2$ ,  $0.8$  and  $1.0 \text{ kg ha}^{-1}$  ( $3.6$ ,  $2.4$  and  $3.0 \text{ kg ha}^{-1}$  of  $\text{SO}_4^{2-}$ ) respectively.

Figure 13 gives the annual total deposition of sulphur. The pattern of annual total deposition of sulphur was sporadic and similar to that of the total wet deposition of sulphur, suggesting that wet deposition was at least as significant as, if not more than, dry deposition to the total mass deposition and acid deposition pattern. Locations of maximum total deposition of sulphur were exactly as those of maximum wet deposition. The amounts of these maxima were  $2.2$ ,  $1.4$ , and  $2.0 \text{ kg ha}^{-1}$  ( $6.6$ ,  $4.2$  and  $6.0 \text{ kg ha}^{-1}$  of  $\text{SO}_4^{2-}$ ) near Whitecourt-Hinton, Fort McMurray and Edson.



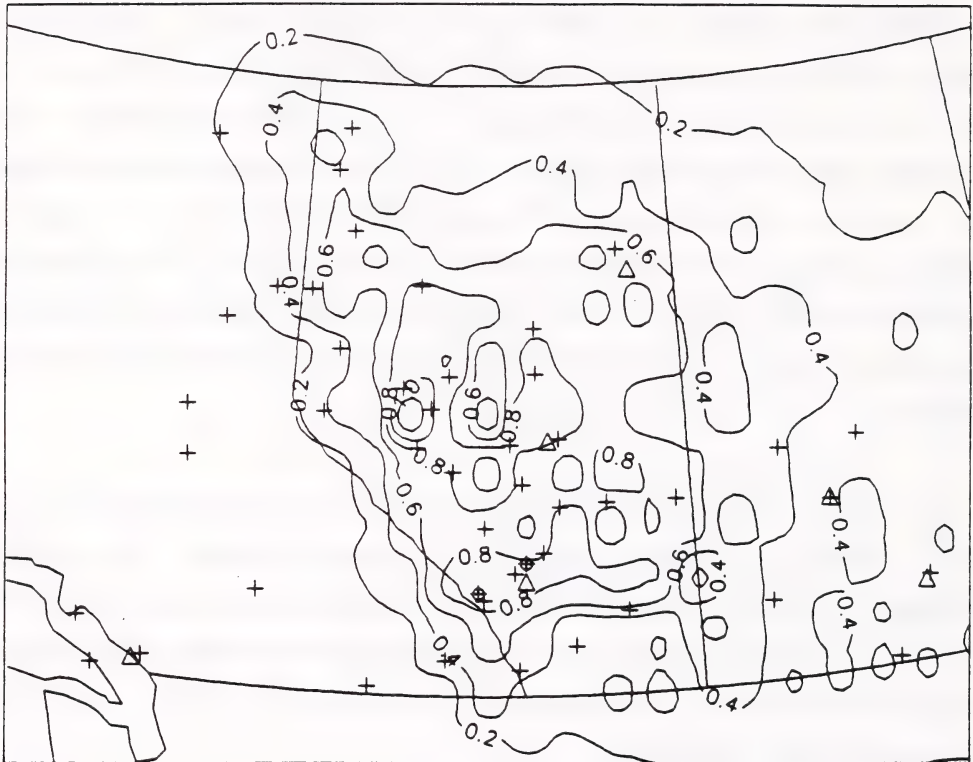


Figure 12. Predicted annual wet deposition of sulphur ( $\text{kg ha}^{-1}$ ). +'s denote locations of emission source and  $\Delta$ 's are major cities.

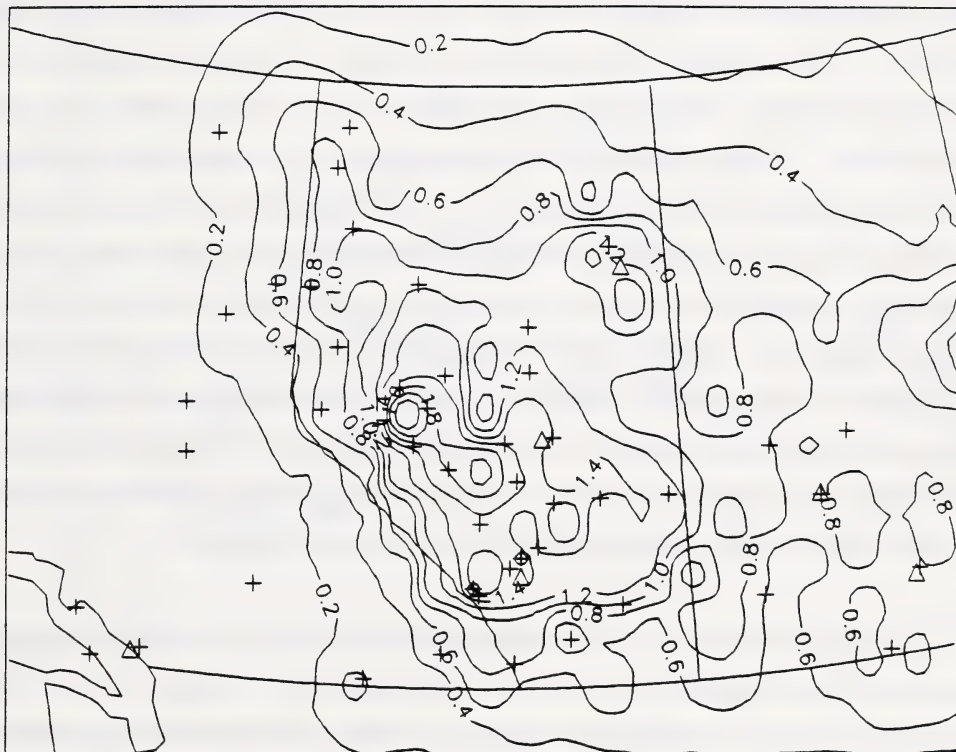


Figure 13. Predicted annual total deposition of sulphur ( $\text{kg ha}^{-1}$ ). '+'s denote locations of emission source and  $\Delta$ 's are major cities.

Monthly dry and wet depositions of sulphur dioxide and sulphate, and total deposition of sulphur in Alberta are presented in Figure 14. Less than one kilotonne of sulphur was deposited per month over the whole province of Alberta in winter. Alberta total deposition of sulphur in the spring and fall increased to 5 to 10 kilotonnes per month. In the summer, total deposition of sulphur in the province was 8 to 14 kilotonnes per month. Monthly total dry deposition of  $\text{SO}_2$  in Alberta varied only in the winter months. The total amount of  $\text{SO}_2$  dry deposition in the winter months differed from those in the other months by almost an order of magnitude. Monthly total dry deposition of sulphate in Alberta was lowest in the December and was highest in May. The variation among monthly total dry deposition of sulphate was not as large as that in  $\text{SO}_2$  dry deposition. Monthly total wet depositions of sulphur dioxide and sulphate were highest in the summer, differing by as much as two orders of magnitude. Although the same wet deposition rate constants were used for months from March to November, wet depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  in the summer months were higher than other months of the year because of the wet summer season.

Figure 15 shows the monthly percentages of emissions from British Columbia, Alberta and Saskatchewan-Manitoba that were deposited in Alberta. In the winter months less than 5% of emissions in Alberta and British Columbia were deposited in Alberta. Note that total emissions in British Columbia were about one quarter of that in Alberta. The deposition in Alberta which originated from British Columbia was about one quarter as well. The percentages of emissions deposited in Alberta increased to 20 to 30% and 15 to 20% of emissions in spring for Alberta and British Columbia respectively. In the summer months, the percentages increased tremendously, in the range of 55 to 75% of emissions from Alberta and 25 to 40% of emissions from British Columbia. In the autumn months, more emissions were transported out. Only 10 to 15% of emissions from both provinces were deposited in Alberta. The contribution of transport from Saskatchewan-Manitoba emission sources

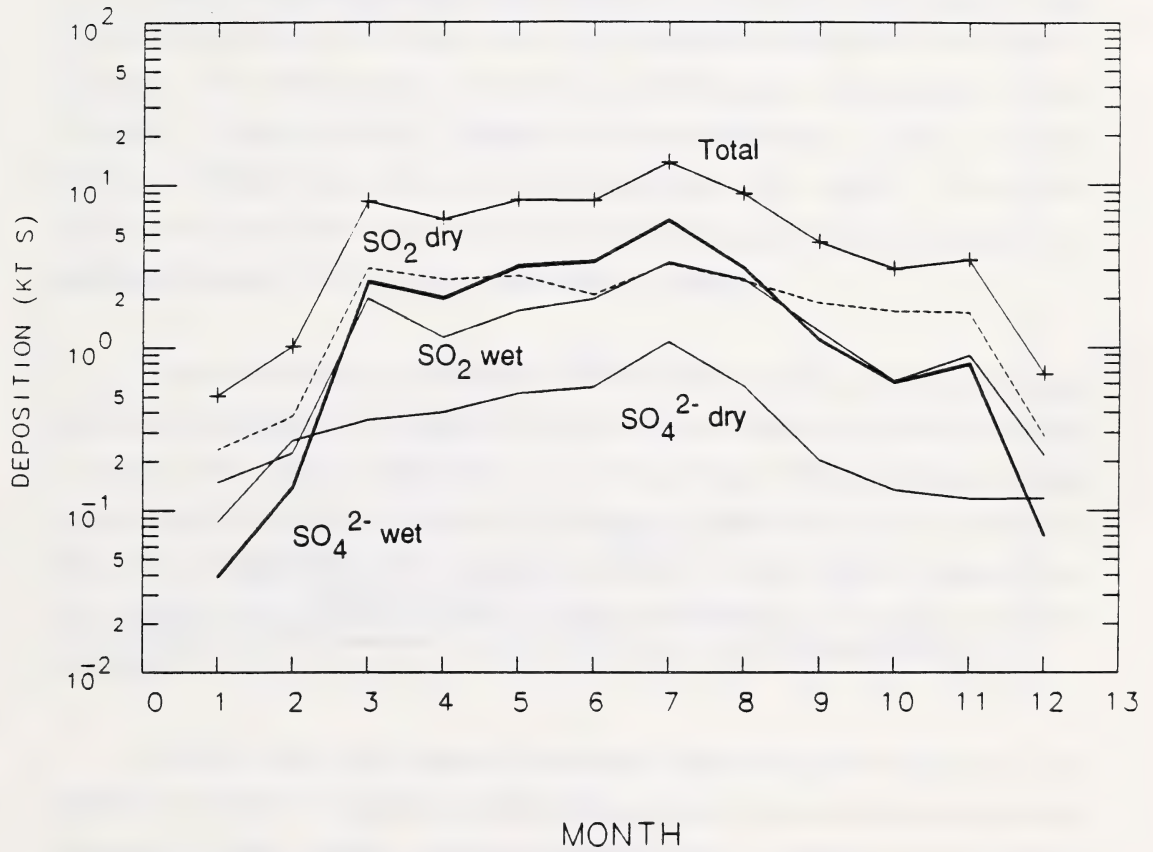


Figure 14. Predicted monthly dry and wet deposition of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, and total S deposition in Alberta (kt of S).



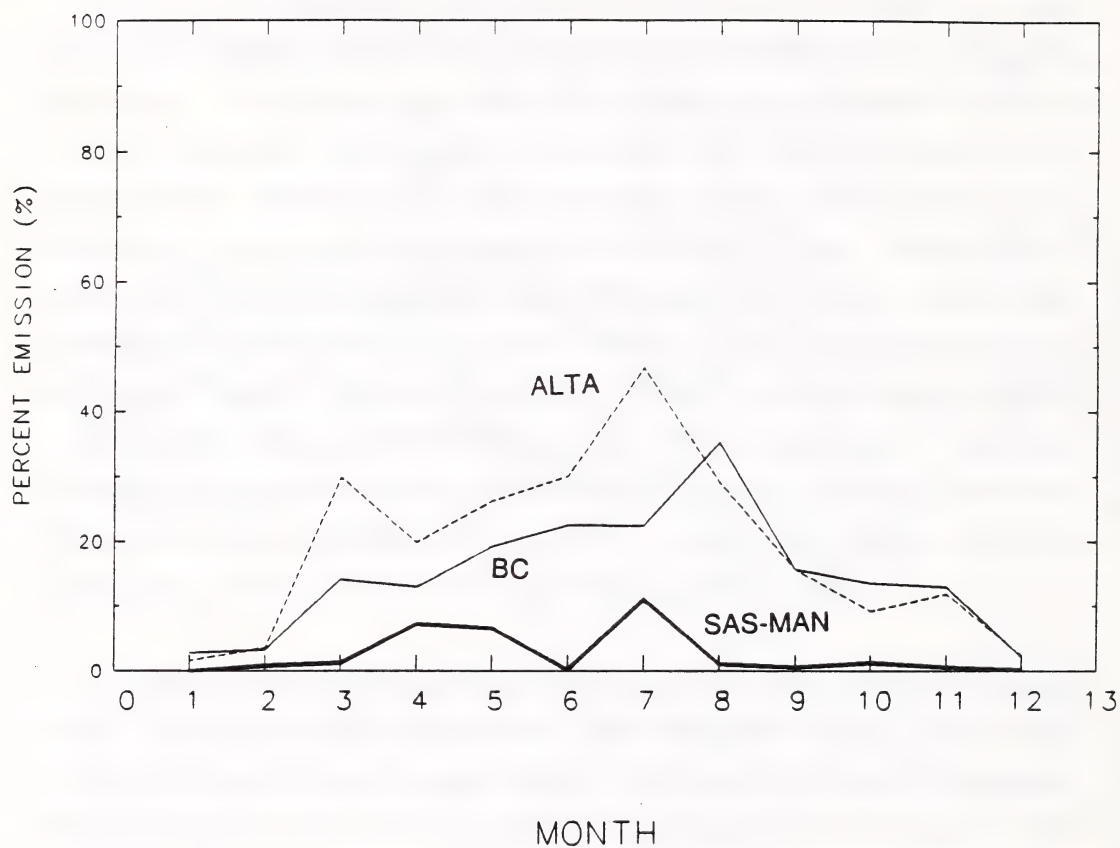


Figure 15. Predicted percentages of emissions from British Columbia, Alberta and Saskatchewan-Manitoba that were deposited in Alberta for 1987.

Saskatchewan-Manitoba emissions deposited in Alberta was less than 8%.

The monthly percentages of total deposition of sulphur in Alberta which were originated from British Columbia, Alberta and Saskatchewan-Manitoba are shown in Figure 16. Over 70% of sulphur depositions in Alberta came from emission sources in Alberta. Emission sources in British Columbia contributed 7 to 28% of sulphur loadings in Alberta, depending upon the meteorology of the month. On the other hand, contributions from emission sources in Saskatchewan-Manitoba ranged from negligible to about 15% of sulphur depositions in Alberta.

The contributions of emissions from the three regions (British Columbia, Alberta, and Saskatchewan-Manitoba) to the various components of sulphur loadings in Alberta were given in Figures 17 to 20. Although the percentages varied considerably from month to month and component to component, 55% in sulphate wet deposition in January and 95% in SO<sub>2</sub> wet deposition in July, Alberta emissions were the dominant contributors for sulphur loadings in Alberta in all forms of sulphur deposition.

The dry to wet ratio of sulphur depositions in Alberta is given in Figure 21. Dry depositions of sulphur were higher than wet depositions near major emission sources (foothills at central Alberta and Fort McMurray) and in southern Alberta where precipitation is infrequent. The largest ratios was 1.7 in the Edson region. Elsewhere, wet depositions were higher than the dry, with the extreme of the dry/wet ratio <0.4 at the northwest corner of the province.

### 3.2 SENSITIVITY TESTS FOR WET DEPOSITION

To assess the importance of the wet deposition rate constants on the sulphur

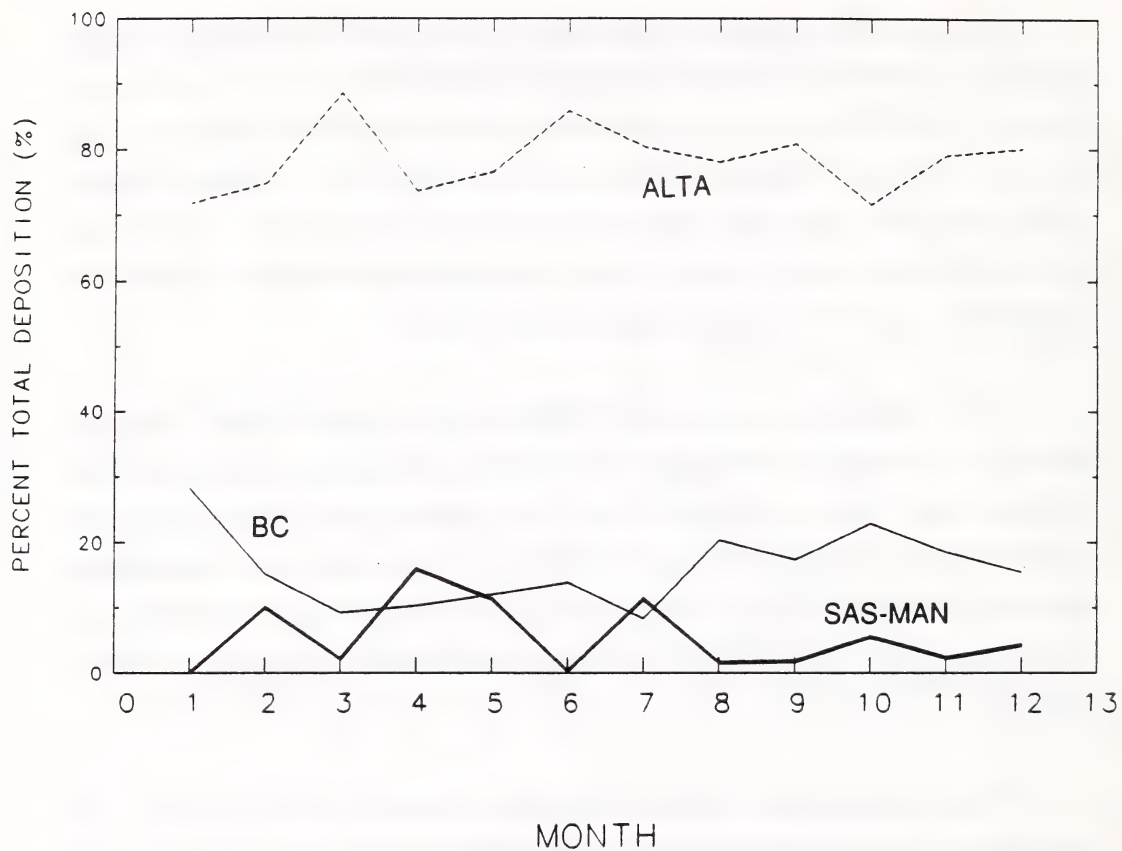


Figure 16. Predicted percentages of total deposition of sulphur in Alberta originating from British Columbia, Alberta and Saskatchewan-Manitoba.

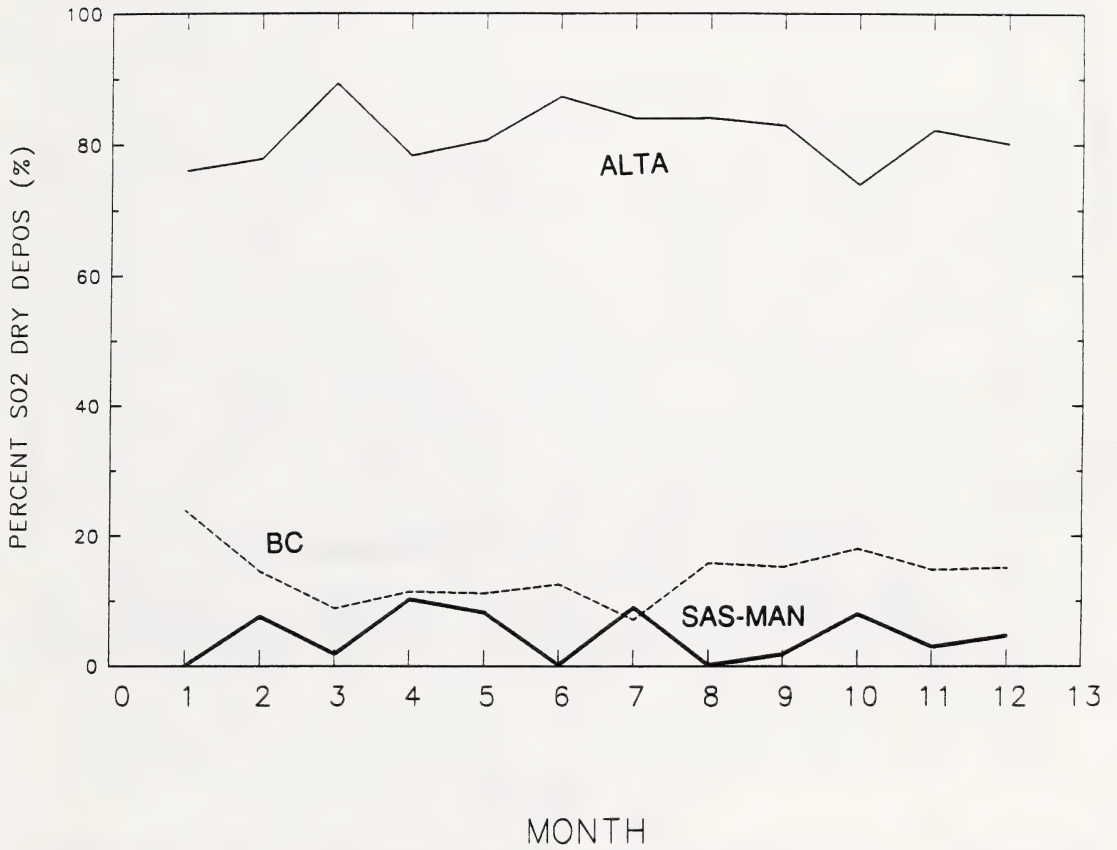


Figure 17. Predicted percentages of dry deposition of SO<sub>2</sub> in Alberta originating from British Columbia, Alberta and Saskatchewan-Manitoba.



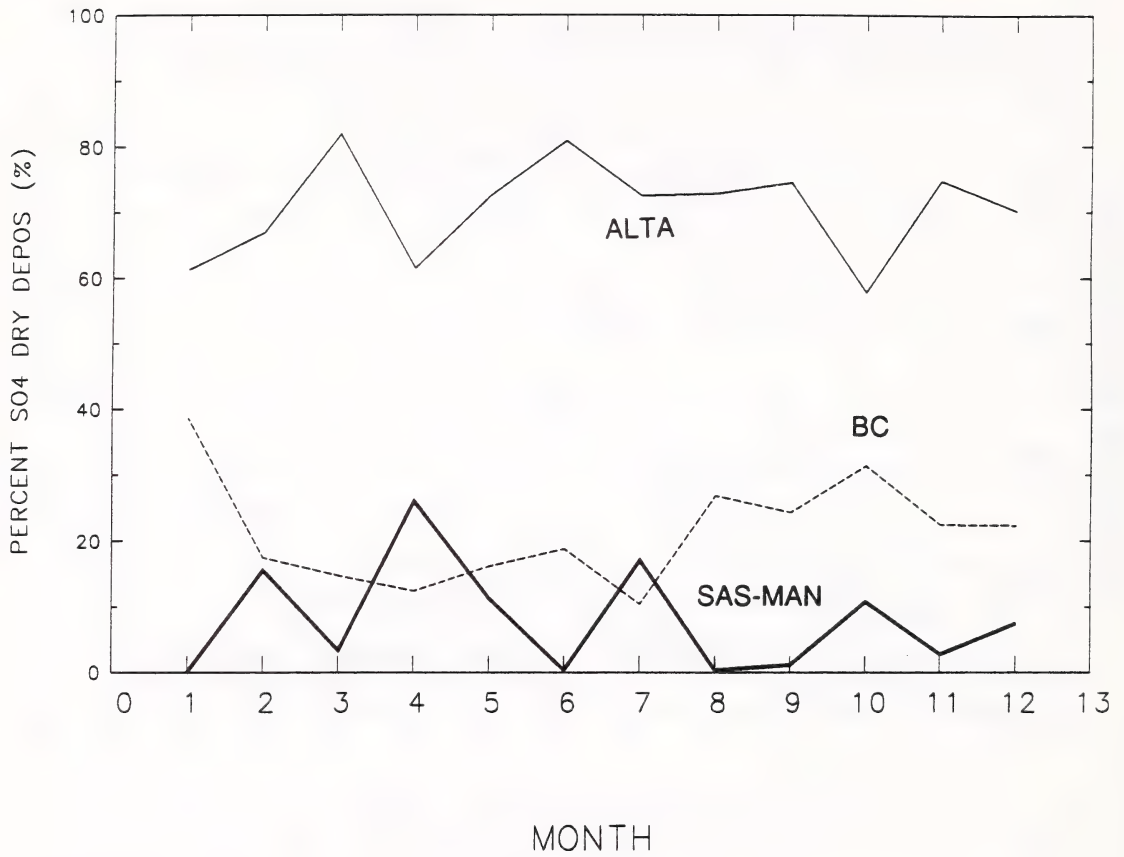


Figure 18. Predicted percentages of dry deposition of  $\text{SO}_4^{2-}$  in Alberta originating from British Columbia, Alberta and Saskatchewan-Manitoba.

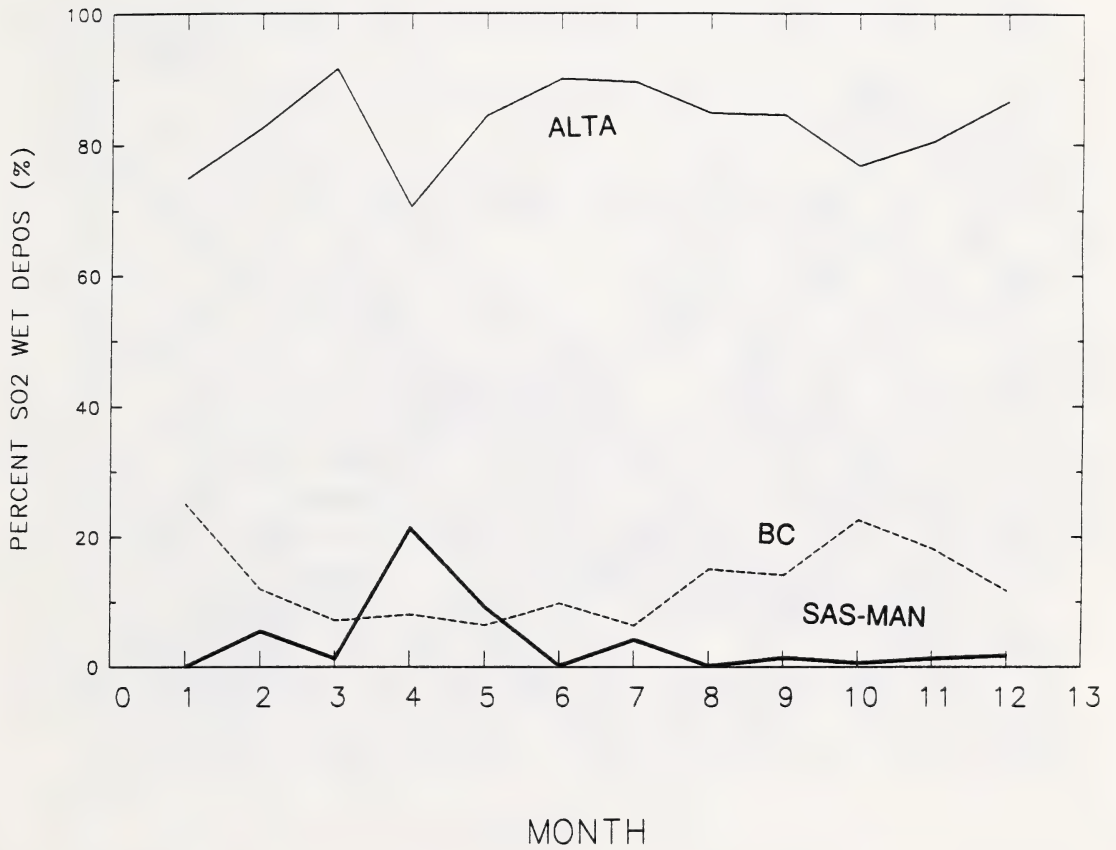


Figure 19.

Predicted percentages of wet deposition of SO<sub>2</sub> in Alberta originating from British Columbia, Alberta and Saskatchewan-Manitoba.

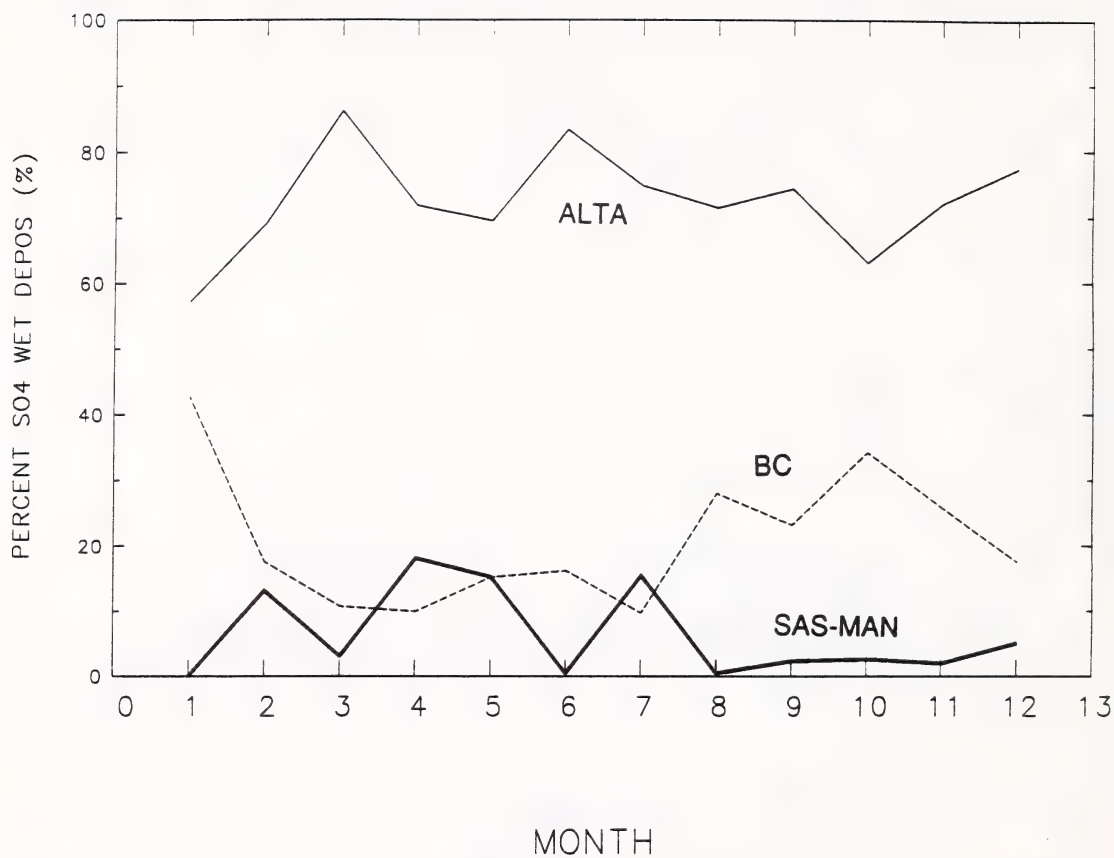


Figure 20. Predicted percentages of wet deposition of  $\text{SO}_4^{2-}$  in Alberta originating from British Columbia, Alberta and Saskatchewan-Manitoba.



Figure 21. Predicted annual ratio of dry/wet deposition of sulphur. +'s denote locations of emission source and Δ's are major cities.



loadings in Alberta, the simulations for summer months have been redone with the default summer wet deposition rate constants.

The distributions of ground level annual mean  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations calculated using the default wet deposition rate constants for the summer months were almost identical as those shown earlier. Maximum  $\text{SO}_2$  annual concentrations were slightly higher, in particular near the oil sands plants at Fort McMurray. In general, the simulated sulphate concentrations were lower everywhere in Alberta, if the default rate constants were used. Similar to the patterns of concentrations, the distributions of dry depositions of  $\text{SO}_2$  and sulphate calculated using the default rate constants for summer months resembled those presented earlier. The differences in the predicted amounts of annual  $\text{SO}_2$  dry depositions in Alberta, using the different wet scavenging ratios for summer months, were minimal. However, the annual dry depositions of sulphate calculated using the default wet deposition rate constants for the summer months were a factor of 1.5 lower everywhere in Alberta than those using the default seasonal values.

If the default empirical constants for  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  for wet deposition rate calculation were used for the summer months, considerable differences resulted in the distributions of the annual wet depositions of  $\text{SO}_2$  and sulphate in Alberta (Figures 22 and 23). The patterns of annual wet depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  remained to be sporadic, because of the isolated nature of precipitation events in the prairies. In general the annual wet depositions of  $\text{SO}_2$  were higher by about a factor of two everywhere in the province. The discrepancies between wet depositions of sulphate calculated using the different constants were not as large as those in the wet depositions of  $\text{SO}_2$ . Except at the Whitecourt-Hinton area where there was a factor of 1.5 difference, the simulated annual wet depositions of  $\text{SO}_4^{2-}$  calculated using the default summer wet deposition rate constants were just slightly higher than that

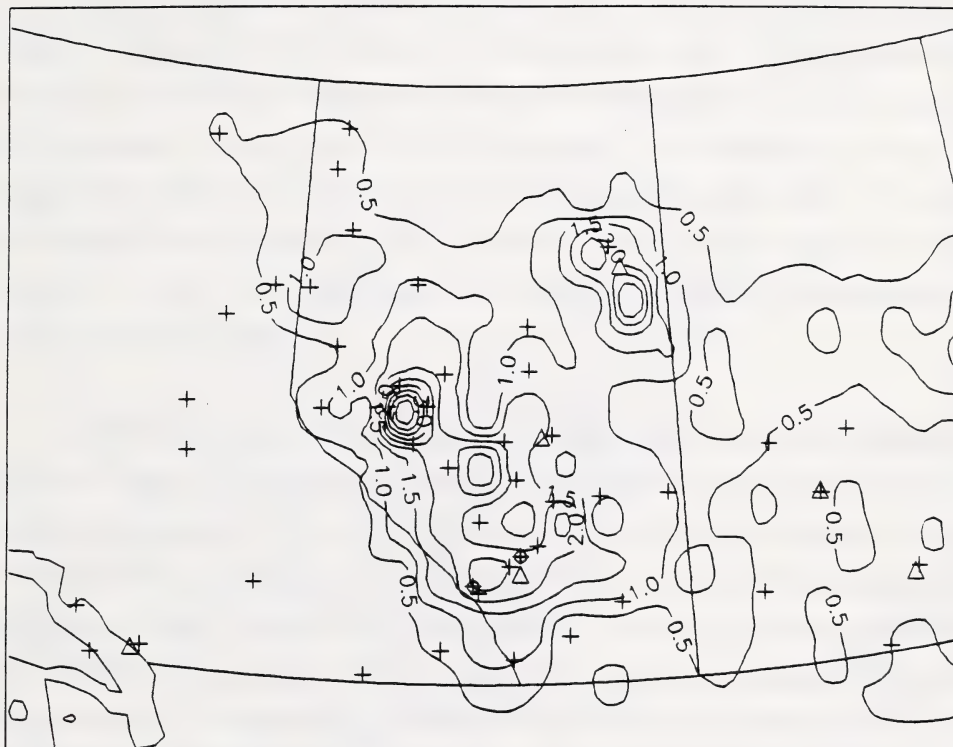


Figure 22. Predicted annual SO<sub>2</sub> wet deposition (kg ha<sup>-1</sup>) using default summer wet deposition rate constants for summer months. Symbols are same as in Figure 10.

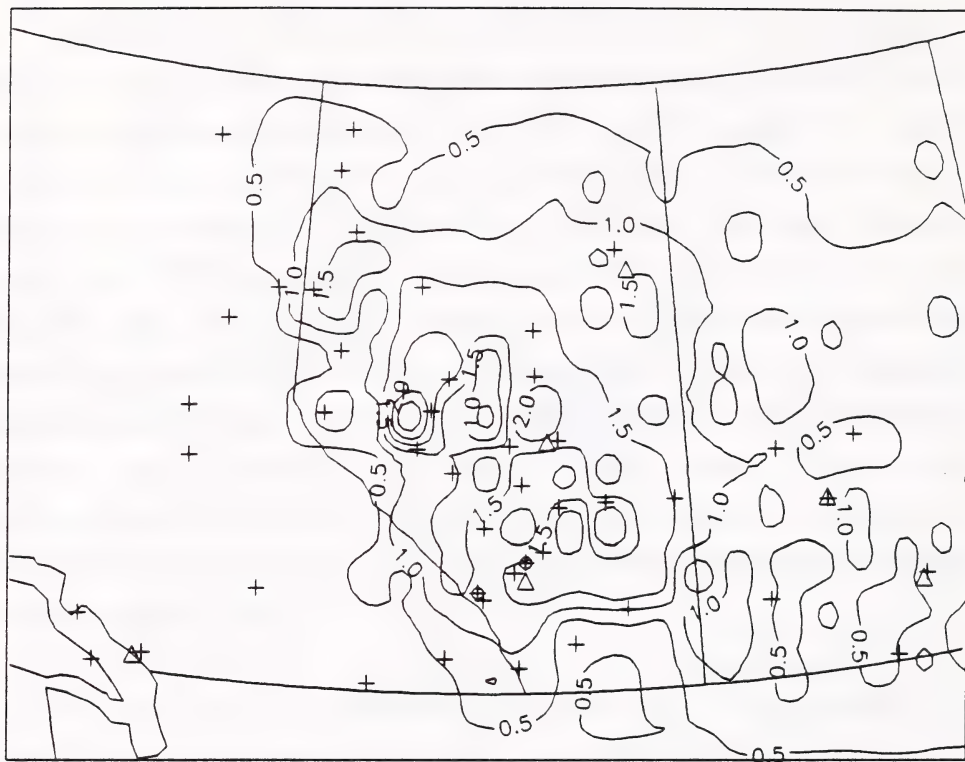


Figure 23. Predicted annual  $\text{SO}_4^{2-}$  wet deposition ( $\text{kg ha}^{-1}$ ) using default summer wet deposition rate constants for summer months. Symbols are same as in Figure 11.

computed using the default spring/fall values for summer months.

Figure 24 gives the annual total deposition of sulphur calculated using the default wet deposition rate constants for the summer months. Unlike the distribution of annual total deposition of sulphur shown earlier, the patterns of concentrations and dry depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  were retained. It appears that dry and wet depositions provide equal contributions to the total deposition of sulphur. The amount of maximum total deposition of sulphur were 4.0, 2.5 and 3.0  $\text{kg ha}^{-1}$  (12.0, 7.5 and 9.0  $\text{kg ha}^{-1}$  of  $\text{SO}_4^{2-}$ ) near Whitecourt, Fort McMurray and Edson areas respectively, same areas shown earlier.

Monthly dry and wet depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , and total deposition of sulphur in Alberta calculated with the default wet deposition rate constants for summer months are presented in Figure 25. In the summer months total deposition of sulphur in the province was 15 to 20 kilotonnes per month. Wet and dry depositions of  $\text{SO}_2$  contributed almost equally to the total deposition of sulphur, while wet deposition of  $\text{SO}_4^{2-}$  was lower by a factor of 1.2 in August to 1.8 in July. The contribution of dry deposition of  $\text{SO}_4^{2-}$  to the total deposition of sulphur was significantly higher than the other components, at least by a factor of 5, except during the winter months.

The monthly percentages of emission from British Columbia, Alberta and Saskatchewan-Manitoba that were deposited in Alberta simulated with the default summer wet deposition rate constants for the summer months are given in Figure 26. The new percentages of emission from Alberta that were deposited in Alberta increased by 22 to 29%. The increase in the percentages of emission from British Columbia that were deposited in Alberta was less drastic, ranging from 2 to 8%. Interestingly, the percentages of emission from Saskatchewan-Manitoba decreased from 5% to 11% in July, but increased slightly in June and August, when the default



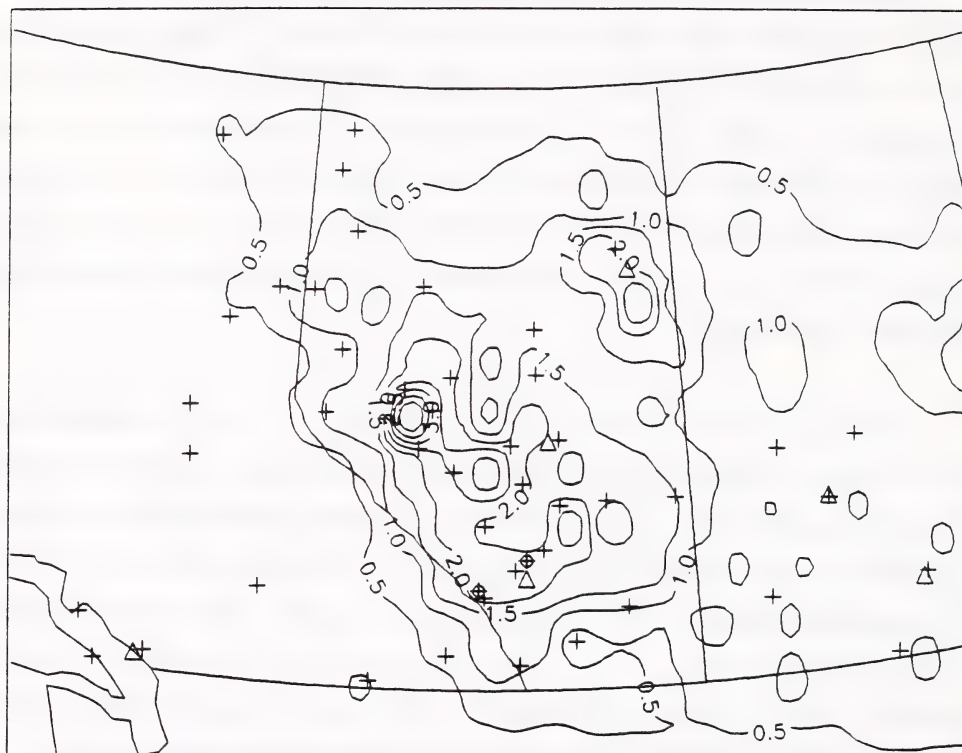


Figure 24. Predicted annual sulphur wet deposition (kg ha<sup>-1</sup>) using default summer wet deposition rate constants for summer months. Symbols are same as in Figure 12.

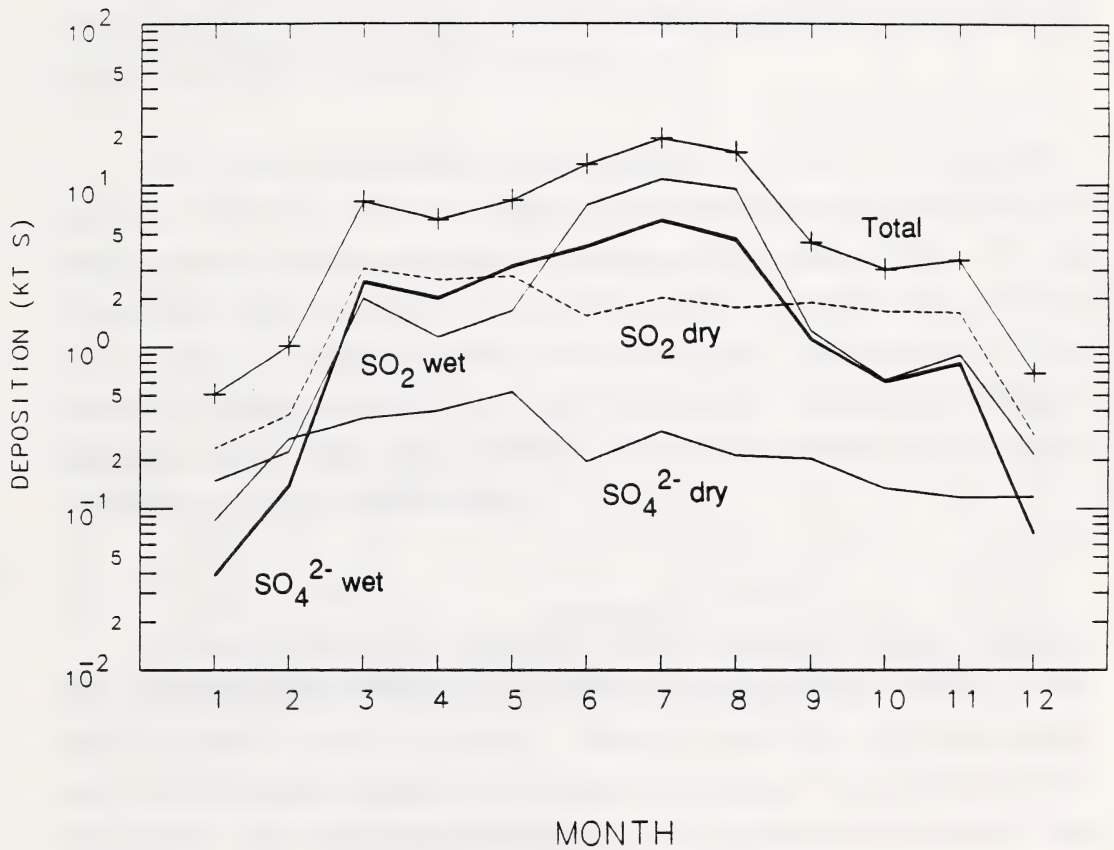


Figure 25. Predicted monthly dry and wet deposition of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> and total sulphur (kt of S) in Alberta using default summer wet deposition rate constants for summer months.

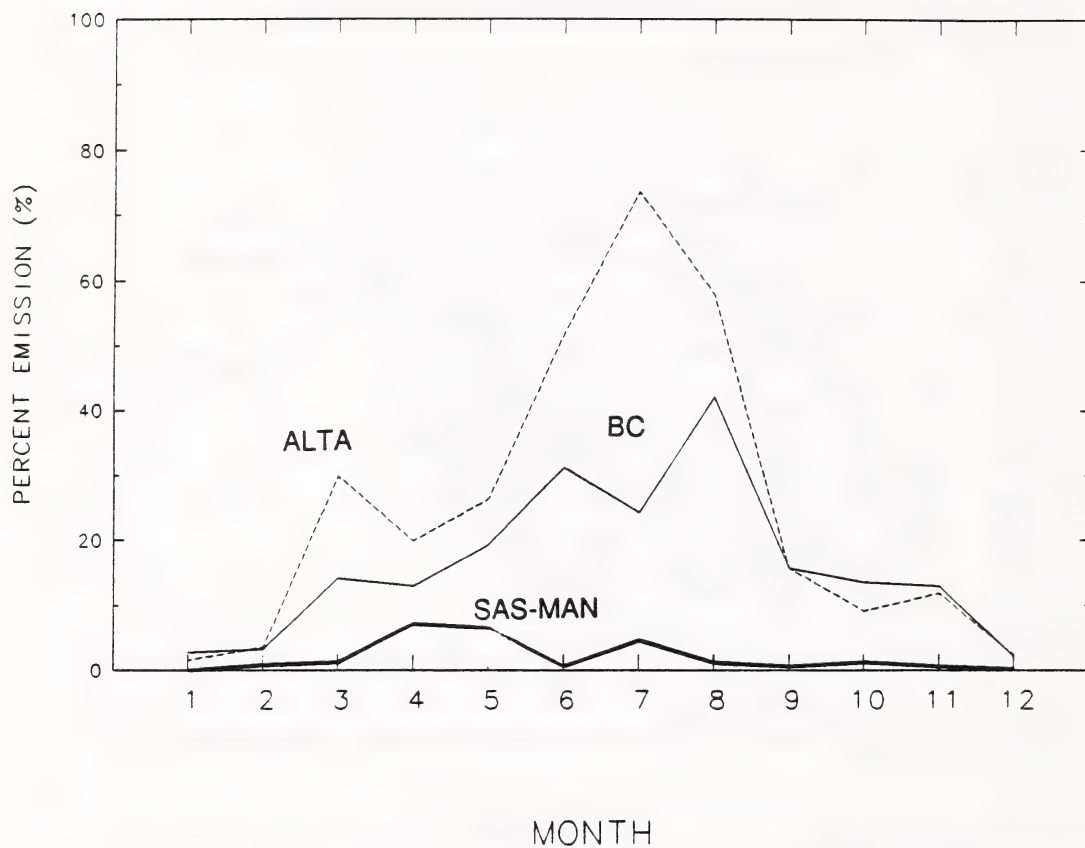


Figure 26.

Same as Figure 15 but calculated using default summer wet deposition rate constants for summer months.

wet deposition rate constants were used in wet deposition calculation. Although the percentages of emission from Alberta that were deposited in Alberta increased considerably when the default wet deposition rate constants were used for the summer months, the contributions of Alberta emission sources to the total deposition of sulphur in Alberta increased by merely 3 to 10%.

The monthly percentages of total deposition of sulphur in Alberta which originated from British Columbia, Alberta and Saskatchewan-Manitoba calculated using the default summer wet deposition rate constants are shown in Figure 27. The percentages of total deposition in Alberta that originated from Alberta did not change much in June, but increased by 10% in July and August. The percentages of total deposition in Alberta originated from British Columbia and Saskatchewan-Manitoba decreased slightly, less than 10% each, if the default summer wet deposition constants were used in the calculations.

The distribution of dry to wet ratio of sulphur depositions in Alberta obtained from simulations using the default summer wet deposition rate constants for the summer months is shown in Figure 28. Except for a few spots in southern Alberta and the Edson areas, wet depositions of sulphur were greater than dry depositions all over Alberta. Dry to wet deposition ratios of 0.2-0.4 occurred in most parts of the province. Unlike the simulations using the default spring/fall wet deposition rate constants for the summer months, the dry depositions were lower than those of the wet even in the grid square closest to major emission sources. This was caused mainly by the very high wet depositions of sulphur in the summer months (as shown in Figure 14). This pattern of the dry to wet ratio of deposition of sulphur is not consistent with correct knowledge. The ratios predicted using the model defaults spring/fall wet deposition rate constants for summer months seem to give more



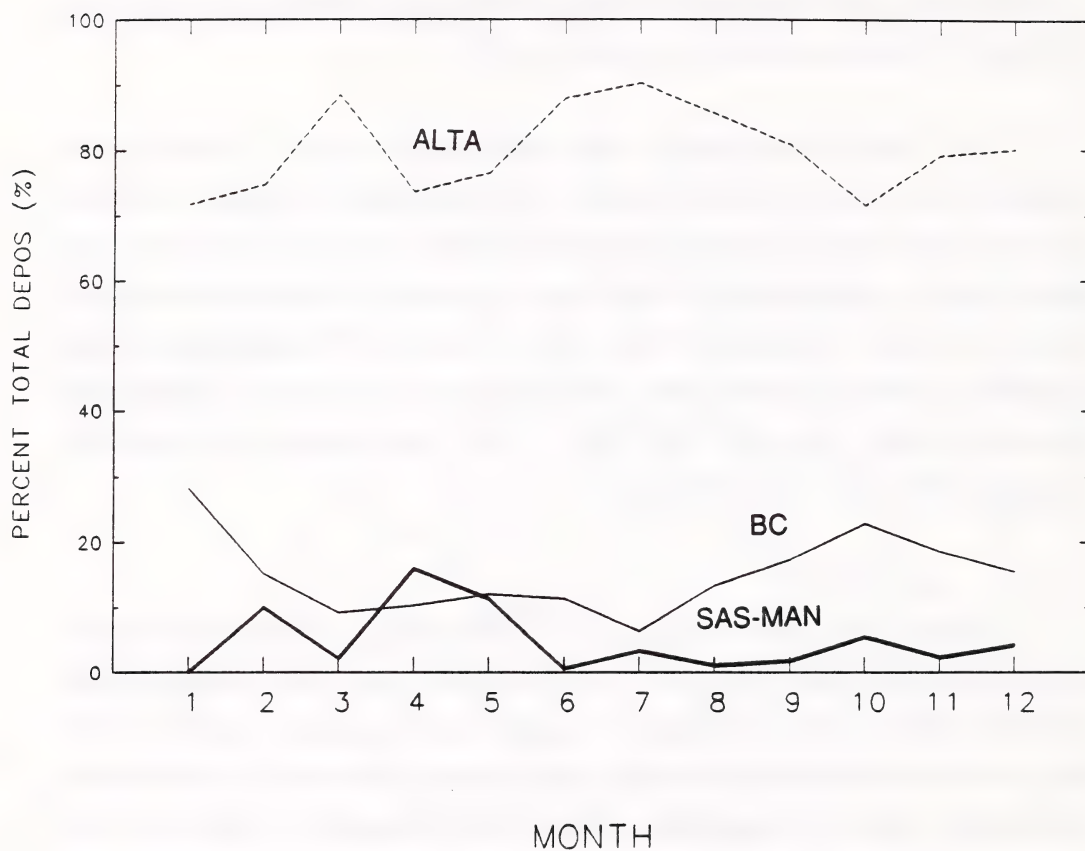


Figure 27. Same as Figure 16 but calculated using default summer wet deposition rate constants for summer months.

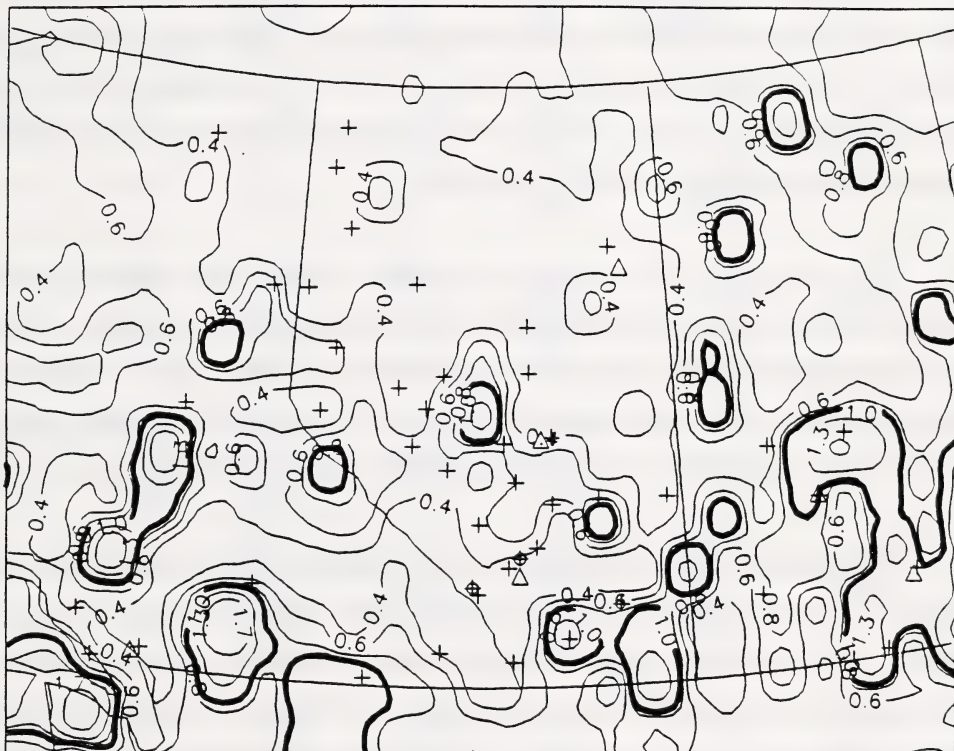


Figure 28. Predicted annual ratio of dry/wet deposition of sulphur calculated using default summer wet deposition rate constants for summer months. Symbols are same as in Figure 21.

realistic results.

RELMAP calculates the total sulphur budget inside the model domain. The seasonal and annual sulphur budgets calculated for the study area are tabulated in Table 5. The normalized budgets are also given. The  $\text{SO}_2$  budgets were normalized by the total emission inputs. The  $\text{SO}_4^{2-}$  budgets were normalized by the amounts of transformation of sulphur dioxide to sulphate.

The dry and wet removals of sulphur dioxide and sulphate and the transformation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  were all low in the winter when compared to those in the other seasons. Thus, the amount of pollutants transported out of the study area was the highest in the winter period. As much as 71% of the  $\text{SO}_2$  emissions and 83% of the sulphate generated were carried out of the study area by winds in the winter.

Precipitation was more frequent in the spring time than in the fall. Hence, the amounts of wet removal, both  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , were larger in the spring than in the autumn. For the same reason, heterogeneous conversion of sulphur dioxide to sulphate occurred more often and, therefore, the amount of  $\text{SO}_2$  transformed was larger in the spring than in the autumn. The dry deposition in the spring time was also higher than that in the fall, probably due to the more unstable atmosphere. As a result, there were 43% of the primary pollutant and 57% of the secondary pollutant transported out of the model's domain in the spring, while there were 59% and 70%, respectively, in the fall.

The summer sulphur budgets from simulations using the default summer (designated by "W" in Table 5) and the default spring/fall (designated by "B") wet deposition rate constants for the summer months are presented. Significantly different budgets were obtained by changing the wet deposition rate constants. Not only was

Table 5. Seasonal and annual sulphur budgets (kt of S) in 1987 for the model domain. The normalized budgets (%) are given in parentheses.

Season	Pollutant	Wet Removal	Dry Removal	Left Domain	Remain in Puff	Trans-formed
Winter	SO <sub>2</sub>	1.29 (1.1)	4.24 (3.4)	88.04 (70.7)	3.22 (2.6)	27.67 (22.2)
	SO <sub>4</sub> <sup>2-</sup>	0.71 (2.6)	2.23 (8.1)	22.98 (83.0)	1.74 (6.3)	
Spring	SO <sub>2</sub>	8.05 (6.4)	18.45 (14.5)	54.43 (42.8)	1.76 (1.4)	44.37 (34.9)
	SO <sub>4</sub> <sup>2-</sup>	14.84 (33.5)	3.55 (8.0)	25.34 (57.1)	0.64 (1.4)	
Summer (B)	SO <sub>2</sub>	13.93 (11.0)	17.32 (13.6)	39.90 (31.4)	1.99 (1.6)	53.77 (42.4)
	SO <sub>4</sub> <sup>2-</sup>	25.24 (46.9)	5.71 (10.6)	21.54 (40.1)	1.27 (2.4)	
Summer (W)	SO <sub>2</sub>	49.62 (39.1)	11.32 (8.9)	28.40 (22.4)	0.27 (0.2)	37.30 (29.4)
	SO <sub>4</sub> <sup>2-</sup>	29.38 (78.7)	1.75 (4.7)	6.07 (16.3)	0.12 (0.3)	
Autumn	SO <sub>2</sub>	5.99 (4.8)	13.67 (10.9)	74.03 (58.9)	0.22 (0.2)	31.63 (25.2)
	SO <sub>4</sub> <sup>2-</sup>	7.43 (23.5)	2.07 (6.5)	22.08 (69.8)	0.05 (0.2)	
Annual (B)	SO <sub>2</sub>	29.27 (5.9)	53.67 (10.6)	256.40 (50.9)	7.19 (1.4)	157.43 (31.2)
	SO <sub>4</sub> <sup>2-</sup>	48.22 (30.6)	13.56 (8.6)	91.94 (58.4)	3.71 (2.4)	
Annual (W)	SO <sub>4</sub>	64.96 (12.9)	47.78 (9.4)	244.90 (48.6)	5.47 (1.1)	140.96 (28.0)
	SO <sub>4</sub> <sup>2-</sup>	52.36 (37.2)	9.59 (6.8)	76.46 (54.2)	2.55 (1.8)	



the amount of wet removals affected, the amounts of dry removals, transformation and transport of primary and secondary pollutants were affected as well. The default summer wet deposition rate constants represent a more efficient removal mechanism. When the summer default wet deposition rate constants were used, 39% of  $\text{SO}_2$  and 79% of  $\text{SO}_4^{2-}$  were removed by wet deposition. If the default spring/fall values were used for the summer months, 11% of  $\text{SO}_2$  and 47% of  $\text{SO}_4^{2-}$  were scavenged by precipitation. Greater wet removal means that the amounts of pollutants available for dry deposition, transformation and transport are reduced. Nevertheless, the amounts of pollutants carried out of the study area by winds were the lowest in the summer period when compared with those of the other seasons, regardless of which wet deposition rate constants were used in the simulations.

Annually, except for the amounts of wet removal of  $\text{SO}_2$ , the sulphur budgets from simulations using the default summer and the default spring/fall wet deposition rate constants for the summer months were very similar. Wet removal of  $\text{SO}_2$  was 6 to 13% of the total amount of emissions, depending upon which wet deposition rate constants were used for the summer months. There were about 10% of  $\text{SO}_2$  removed as dry deposition, 50% transported out of the study area, 1% remained in puffs (suspended in air within the model's domain), and 30% transformed to  $\text{SO}_4^{2-}$ . At the same time, about 30 to 35% of  $\text{SO}_4^{2-}$  converted from  $\text{SO}_2$  were removed as wet deposition, 7 to 9% taken off as dry deposition, 55 to 60% carried out of the study area by winds, and 2% remained in puffs.



#### 4. DISCUSSION

A preliminary estimate of sulphur loadings in Alberta has been generated using the REgional Lagrangian Model of Air Pollution (RELMAP) and the contributions of transport from out-of-the-province sources to the sulphur depositions in Alberta have been determined. The 1987 meteorological data and the 1984 sulphur emission inventory were used. The simulation results have been presented in the previous section. In this section, the simulation results will be assessed based on available data or results from earlier similar studies.

RELMAP is a regional scale model with a resolution of  $1^{\circ}$  latitude  $\times$   $1^{\circ}$  longitude, or roughly 10,000 km<sup>2</sup>. Furthermore, horizontal diffusion of pollutant puffs in the model is assumed to occur at a constant rate, so that the area of each puff increases at a constant rate, and the pollutant mass in the puff is assumed to be homogeneous in the horizontal plane at all time. RELMAP is not suitable for short-term simulations or calculation of plume impingement within close vicinity of emission sources. The model is not capable of resolving the high concentrations, and, thus, depositions in the immediate vicinity of point sources. Therefore, the simulation results should only be assessed based on the overall regional scale features or compared with measurements from monitoring stations far from the local effects of emissions.

Three long range transport of air pollution statistical models; Fisher (Fisher 1975, 1978), Ontario Ministry of Environment Statistical model (MOE) (Venkatram et al, 1982) and Regional Climatological Dispersion Model (RCDM) (Fay and Rosenzweig, 1980), have been run for western Canada (Thomson, 1990). The meteorological data were compiled for two periods. The first period was from 1974 to 1985 and the second was for 1982. These intervals were chosen to provide

climatologically averaged conditions and specific data for one year for comparison. The emission data used in those simulations were obtained from the same sources as in this study. All three models predicted similar patterns of the concentration of sulphur dioxide over the Prairies, with concentrations predicted by one of the models considerably lower than from the other two, particularly in the vicinity of major point sources (Fort McMurray and Flin Flon). When distribution of concentrations obtained from the present study were compared with the results in that study, the same agreement was achieved. Two locations of maximum concentration of  $\text{SO}_2$  were identified in Alberta: near Fort McMurray and central Alberta along the foothills west of Edmonton and Calgary. The values of  $\text{SO}_2$  concentration simulated by RELMAP fell in between the extremes of the predicted values in the Thomson's study.

Wet and dry depositions of sulphur were also predicted by the three models in the Thomson's study. The distribution of the annual wet sulphur deposition predicted by these models was fairly smooth and followed the same general pattern as those of sulphur dioxide concentrations, because these models use simple composite meteorology and the mean length of wet and dry periods in calculating the wet deposition of sulphur. The pattern of wet deposition of sulphur simulated by RELMAP, on the other hand, was very spotty because precipitation events were considered. Nevertheless, the magnitude of wet deposition of sulphur in Alberta estimated by RELMAP was quite similar to those predicted by the three statistical models.

In the Alberta Government/Industry Acid Deposition Research Program (ADRP), the Climatological Dispersion Model (CDM) (Busse and Zimmerman 1973) has been applied to estimate the seasonal and annual average concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_x$  in Alberta. A very detailed emission inventory for  $\text{SO}_2$  sources in Alberta was included in the application. Estimated background concentrations of 0.5

$\mu\text{g m}^{-3}$  for sulphur dioxide and  $0.4 \mu\text{g m}^{-3}$  for sulphate were also used to account for the presumably small transport into the Province from outside sources. The meteorological data were extracted from the input database prepared for the three statistical long range transport of air pollutant models study mentioned earlier. The model also predicted maximum annual concentrations of  $\text{SO}_2$  near the oil sands plants at Fort McMurray and near Edmonton, Calgary, and areas in between. However, the values of concentration were at least 2 to 3 times higher than those predicted by the three long-range statistical models in Thomson's study and by RELMAP in the present study.

The distributions of concentrations and dry depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  in Alberta as simulated by RELMAP possessed a northwest-southeast orientation. Furthermore, the gradient of contours were larger along the mountain range than towards the prairies. It appears that the considerable large number of surface meteorological stations used in the study has reproduced the topographic effects through detailed wind measurements, even though topography was not considered in the model.

It is difficult to verify the accuracy of the model results presented because of the lack of monitoring data in Alberta which are specifically designed for model evaluation. In ADRP, integrated measurements and computations of annual averaged  $\text{SO}_2$  concentrations were obtained at the Crossfield East, Crossfield West, and Fortress Mountain monitoring sites. The Crossfield East and Crossfield West stations are located among emission sources. Local effects of emission at these sites were significant. In fact, the annual averaged  $\text{SO}_2$  concentrations obtained at the Crossfield East and Crossfield West, which were separated by less than 10 km, were  $5.6$  and  $4.4 \mu\text{g m}^{-3}$ , respectively. Thus, only the measurements at the Fortress Mountain monitoring site are used to assess the model results in this study.



ADRP integrated measurements and computations of annual average  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations at the Fortress Mountain monitoring site indicate values of 1.4 and  $0.5 \mu\text{g m}^{-3}$ , respectively. Model results for the Fortress Mountain area, derived from the data as shown in Figures 6 and 7, are on the order of  $1.3 \mu\text{g m}^{-3}$  for  $\text{SO}_2$  concentration and  $0.3 \mu\text{g m}^{-3}$  for  $\text{SO}_4^{2-}$  concentration. There are substantial natural emissions of sulphur compounds into the troposphere from biological activity in vegetation, soils, and aquatic ecosystems. Tropospheric concentrations of sulphur dioxide and sulphate range from  $0.1$  to  $0.9 \mu\text{g m}^{-3}$  and  $0.1$  to  $0.6 \mu\text{g m}^{-3}$ , respectively, in unpolluted air (Sze and Ko 1980). Since these 'global background' concentrations were not included in the RELMAP simulations, the model results agree remarkably well with those actually observed.

With an estimated deposition velocity of  $0.7 \text{ cm s}^{-1}$  a rate of  $\text{SO}_2$  dry deposition of  $2.9 \text{ kg ha}^{-1} \text{ y}^{-1}$  was calculated from the measured mean  $\text{SO}_2$  concentration at the Fortress Mountain monitoring site in ADRP. The amount of dry deposition given above depends heavily on the accuracy of the dry deposition velocity, which was estimated from data obtained during limited adiabatic periods in February 28 and March 17, 1988. The  $0.7 \text{ cm s}^{-1}$  value of the dry deposition velocity of  $\text{SO}_2$  is considerably higher than the  $0.2$ - $0.3 \text{ cm s}^{-1}$  applied by the Atmospheric Environment Service in studies of dry deposition in Ontario (Barrie and Sirois 1986). Thus, the  $2.9 \text{ kg ha}^{-1} \text{ y}^{-1}$   $\text{SO}_2$  dry deposition may represent the upper limit of dry deposition occurred at Fortress Mountain. The simulated  $\text{SO}_2$  dry deposition by RELMAP at Fortress Mountain area was  $1.1 \text{ kg ha}^{-1} \text{ y}^{-1}$ . Considered the uncertainties involved, the model result was in reasonable agreement with the  $\text{SO}_2$  dry deposition value estimated from the Fortress Mountain monitoring value.

Sulphate wet deposition measured at the Fortress Mountain monitoring site was  $2.4 \text{ kg ha}^{-1} \text{ y}^{-1}$  of sulphur. Since  $\text{SO}_2$  in water rapidly oxidizes to  $\text{SO}_4^{2-}$ , the

simulated wet deposition of total sulphur should be used to compare with the measured value. RELMAP estimated that the wet deposition of sulphur at Fortress Mountain area was about  $0.9 \text{ kg ha}^{-1} \text{ y}^{-1}$ . As stated earlier that 'global background' was not included in this study, the simulated wet deposition should be considered in reasonable agreement with the monitoring result. If the background  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations were assumed to be  $0.5$  and  $0.35 \mu\text{g m}^{-3}$  respectively, the mid-values suggested by Sze and Ko (1980) for unpolluted air, the wet deposition of sulphur at Fortress Mountain became  $1.7 \text{ kg ha}^{-1}$ .

Monthly, seasonal, and annual average concentrations and accumulative depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  in Alberta have been estimated through the application of the RELMAP model. As shown in Table 6, the CPU usage on the VAX 6210 computer system for the simulations in this study varied considerably. The computational requirements of running RELMAP vary with the simulation period, domain area, meteorology, and number and rate of emission. Since the domain area, number of emission source (49) and rates of emission were fixed, the variation in the computational demand was caused mainly by the monthly weather.

Table 6. CPU usage for the 1987 simulations on the VAX 6210 computer system.

Month	CPU (min)	Month	CPU (min)
January	50	July	128
February	48	August	70
March	64	September	49
April	55	October	40
May	63	November	36
June	56	December	63



Modelling results were in reasonable agreement with existing data and appeared to provide a realistic overview of average pollutant exposure in Alberta. However, the model should be further evaluated and verified using field data collected specifically for model evaluation use and emission inventory covered the whole model's domain. Furthermore, although efforts were made to use model parameters which were appropriate for the geographic domain of the model, most of the parameters used were derived empirically and generalized from laboratory experiments and limited site measurements for specific but limited conditions and geographical regions. It has been shown that altering the wet deposition rate constants for the summer month simulations, the overall outcomes could be greatly affected. Thus, before performing rigorous evaluations and applications for impact assessment RELMAP should be calibrated using available measurements, so that input parameters used in the model are appropriate for the study area.

## 5. CONCLUSIONS AND RECOMMENDATIONS

To summarize, a preliminary estimate of sulphur loadings in Alberta has been generated using the RELMAP model as a practical mesoscale deposition predictor.

To generate the preliminary estimate of sulphur loadings, the 1987 meteorological data and the 1984 sulphur emission inventory were used. Considering that global background was not included in the RELMAP model, the modelling results were in reasonable agreement with the ADRP measurements at Fortress Mountain. Annual averaged  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations were observed to be  $1.4$  and  $0.5 \mu\text{g m}^{-3}$ , respectively, while RELMAP predicted  $1.3$  and  $0.3 \mu\text{g m}^{-3}$ . Dry deposition of  $\text{SO}_2$  was estimated to be  $2.9 \text{ kg ha}^{-1}$  from measurements and RELMAP predicted a value of  $1.2 \text{ kg ha}^{-1}$ . Wet deposition of sulphate measured at the Fortress Mountain monitoring site and calculated by RELMAP were  $2.4$  and  $0.9 \text{ kg ha}^{-1}$ , respectively. The present study results agreed qualitatively, as well, with a variety of air quality modelling studies performed for Alberta. Thus, the simulation results appeared to provide a reasonably acceptable overview of average concentrations and depositions in Alberta.

Maximum ground level annual averaged  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations in Alberta, of  $1.2$  and  $0.3 \mu\text{g m}^{-3}$ , respectively, were located at the Edson area. Aside from the Edson area, maximum annual concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  were also located near the oil sands plants at Fort McMurray, with values  $1.2$  and  $0.2 \mu\text{g m}^{-3}$ , respectively. The concentration patterns possessed a northwest-southeast orientation. Since emissions of  $\text{SO}_2$  are concentrated in the central Alberta and Fort McMurray regions, these results indicated that the distributions of mean pollutant concentration across Alberta are dictated by source regions and meteorology. Maximum dry depositions of  $\text{SO}_2$  occurred downwind from major emission sources, with values of

1.6 kg ha<sup>-1</sup> along the foothills west of Edmonton and 1.1 kg ha<sup>-1</sup> at Fort McMurray. The annual dry deposition of sulphate within Alberta was, in general, one third to one fifth that of SO<sub>2</sub>. The maximum sulphate dry deposition of 0.2 kg ha<sup>-1</sup> was located at central Alberta, extending from the foothills to the Alberta and Saskatchewan Border and between Edmonton and Calgary. The distributions of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> wet depositions were very sporadic because of the showery nature of the precipitation events in the Prairies. Maximum wet depositions of sulphur near Whitecourt-Hinton, Fort McMurray and Edson areas were 3.5, 2.0 and 2.0 kg ha<sup>-1</sup> of Sulphur or 10.5, 6.0 and 6.0 kg ha<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup>, respectively.

Monthly total dry and wet depositions of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, and total deposition of sulphur in Alberta were lowest in the winter months (December, January and February). Wet depositions were highest in the summer months (June, July and August). Except for the winter months, monthly total dry deposition of SO<sub>2</sub> did not vary significantly. As a whole, total dry deposition of SO<sub>2</sub> contributed more to the sulphur loadings in Alberta than wet SO<sub>2</sub>, dry SO<sub>4</sub><sup>2-</sup> or wet SO<sub>4</sub><sup>2-</sup> in every season, except during the summer.

The contributions of transport to sulphur loadings in Alberta from out-of-the-province emission sources have been determined. The amount of British Columbia emissions deposited in Alberta varied from 2% in the December to 42% in August. Considerable variation also existed in the amount of Alberta emissions deposited in Alberta, ranging from 2% in December to 74% in August. The contribution of transport from Saskatchewan-Manitoba emission sources to sulphur loadings in Alberta was not significant, with maximum less than 8%. Because total emissions in British Columbia were almost one quarter of those in Alberta, over 70% of sulphur depositions in Alberta came from emission sources in Alberta. Emission sources in British Columbia contributed 7 to 28% of sulphur loadings in Alberta, depending upon

the meteorology of the month. Contribution from emission sources in Saskatchewan-Manitoba ranged from negligible to about 15% of sulphur depositions in Alberta.

Significant variation existed in the seasonal sulphur budget inside the modelling domain. There was 71% of emissions transported out of the modelling domain in winter, while only 22% was advected out in summer. Wet removal of  $\text{SO}_2$  varied from 1% in winter to 39% in summer. Dry removal of  $\text{SO}_2$  ranged from 3% in winter to 15% in spring. Transformation of  $\text{SO}_2$  to sulphate ranged from 22% in winter to 35% in spring. Of the sulphate generated from  $\text{SO}_2$  emissions, transport out of the modelling domain ranged from 16% in summer to 83% in winter, wet removal from 3% in winter to 79% in summer, and dry removal from 5% in summer to 8% both in winter and spring. Annually, 13% of the total  $\text{SO}_2$  emissions was removed by wet deposition and 9% by dry deposition, 49% was transported out of the study area, and 28% was converted to  $\text{SO}_4^{2-}$ . At the mean time, about 37% and 7% of  $\text{SO}_4^{2-}$  were removed by wet and dry depositions, respectively, and 54% was transported out of the modelling domain.

Based upon the experience gained in this study, the following specific recommendations are presented:

1. It is recommended that further sensitivity analyses of the RELMAP model be performed. Comparison between RELMAP simulations and existing monthly wet deposition data should be conducted. Data collected at precipitation quality monitoring stations operated by Alberta Environment can be used to fine tune the model. Optimal model parameters, in particular the wet deposition rate constants, which produce the best agreement with observations in Alberta, should be determined. These parameters should be used for future model verification.



2. It is recommended that the field monitoring program includes stations at the location of the maximum predicted deposition - Whitecourt-Hinton and Fort McMurray. Each station should at least be equipped to measure concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , and estimates of dry deposition of total sulphur, as well as wet deposition.
3. The processing of meteorological data is extremely demanding, both in computational time and storage. It requires more disk space and CPU time for extracting and formatting a month's meteorological data than for the RELMAP simulation. Thus, it is recommended that an one-year meteorological period which is representative of the anticipated long-term conditions in Alberta be selected. Future scenario simulations of environmental loadings from projected emissions should be performed on the basis of this climatological representative meteorological data. It should be noted that using an "average" meteorological year will eliminate the effects of a specific condition associated with a particular episodic events. Should this type of application be required, meteorological data connected with such condition must be used in the simulation.
4. A model prediction is only as good as the input data. It is recommended that emissions, together with released conditions, be collected and updated on the time and space scales used by the model.
5. Atmospheric depositions of nitrogen and ammonium compounds contribute significantly to acidic loading also. It is recommended that a coupled simple chemical mechanism of  $\text{SO}_2$ - $\text{NO}_x$ - $\text{NH}_3$  system be incorporated into the RELMAP model.

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## 7. APPENDICES

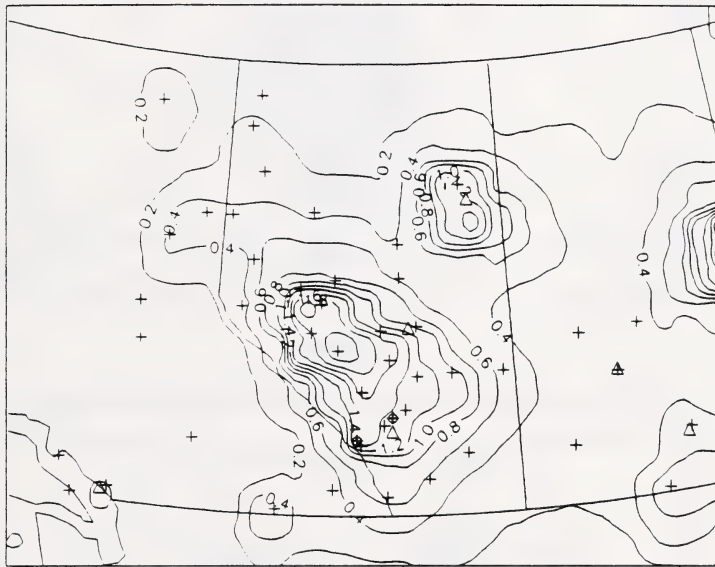
### 7.1 SEASONAL VARIATIONS OF SULPHUR LOADINGS

The seasonal simulations are presented with the purpose of examining the relationship between seasonal meteorological variations and the seasonal averaged ground level concentrations and seasonal amounts of depositions. The results of summer simulations using the default spring/fall wet deposition rate constant are presented, as well as that using the default summer values. Annual emission rates were used in this study. Therefore, the variations in concentrations and deposition depend upon changing patterns of wind flow and precipitation, as well as the model parameter values which change seasonally.

Simulated distributions of seasonal mean concentration of  $\text{SO}_2$  are shown in Figure 29. The patterns were very similar for the four seasons. However, seasonal maximum concentrations differed in values. The distributions of the concentration appear to be determined primarily by the location of sources, with some effect of prevailing meteorology evident in the northwest-southeast orientation of the contours and the maximum values.

Unlike the  $\text{SO}_2$  concentrations, seasonal variation in  $\text{SO}_4^{2-}$  were considerable. The distributions of seasonal averaged concentration of  $\text{SO}_4^{2-}$  are given in Figure 30. The dissimilarity in concentration patterns could be attributed to the transformation rate difference in each season. The conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  was slow in the winter months. Transformation took place further downwind from the  $\text{SO}_2$  emission sources. Whereas, the transformation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  was much faster in summer; the predicted distribution of  $\text{SO}_4^{2-}$  concentration was rather similar to that of  $\text{SO}_2$ .

The distributions of seasonal  $\text{SO}_2$  dry deposition are shown in Figure 31. In summer, unstable weather prevailed. The pattern of  $\text{SO}_2$  dry deposition followed that of the  $\text{SO}_2$  concentration, because of the higher dry deposition velocity. In winter, the boundary layer was characterized with stable weather and the dry deposition velocity was low. Thus, pollutant travelled further downwind before deposited to the surface. The pattern of  $\text{SO}_2$  dry deposition was very different from that of the  $\text{SO}_2$  concentration.

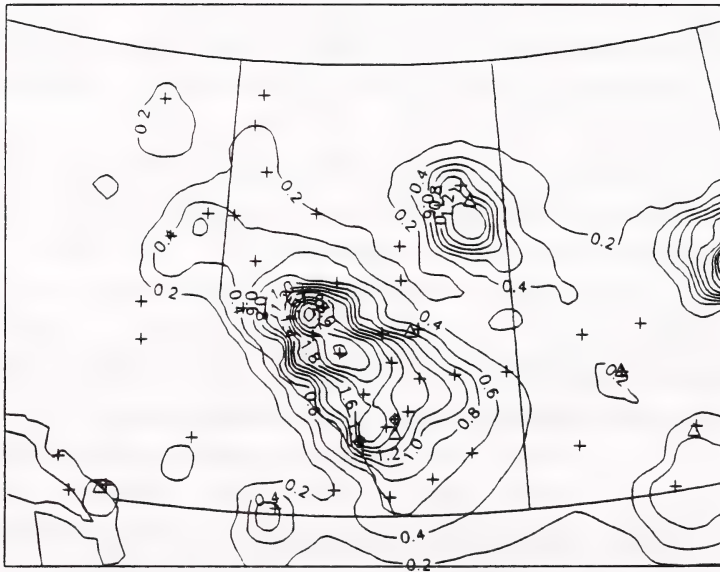


(A)

Figure 29. RELMAP simulated seasonal mean concentration of sulphur dioxide ( $\mu\text{g m}^{-3}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +’s denote locations of emission source and  $\Delta$ ’s are major cities.



(B)

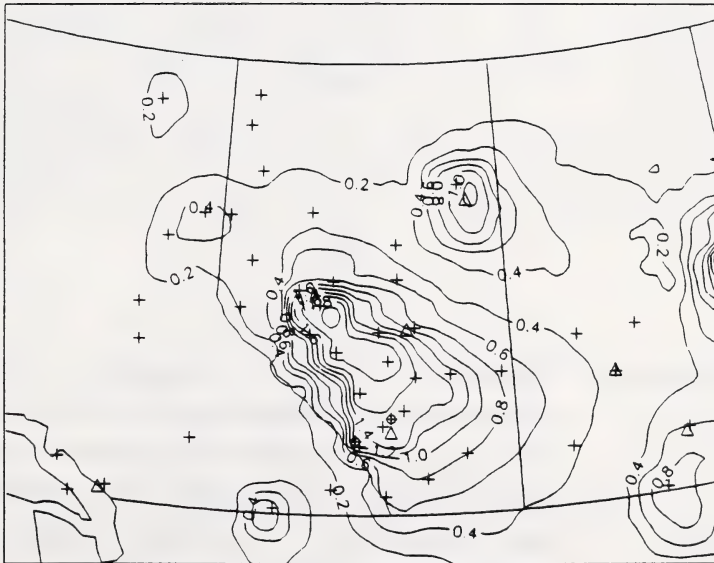


(C)

Figure 29. Continued



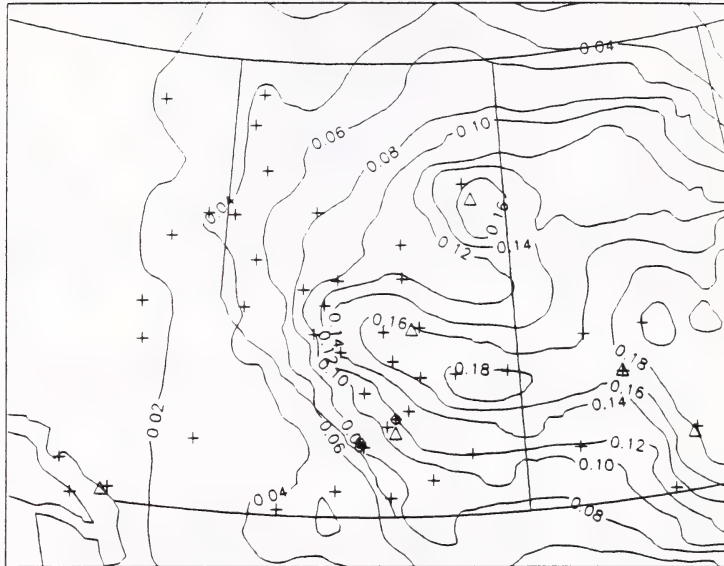
(D)



(E)

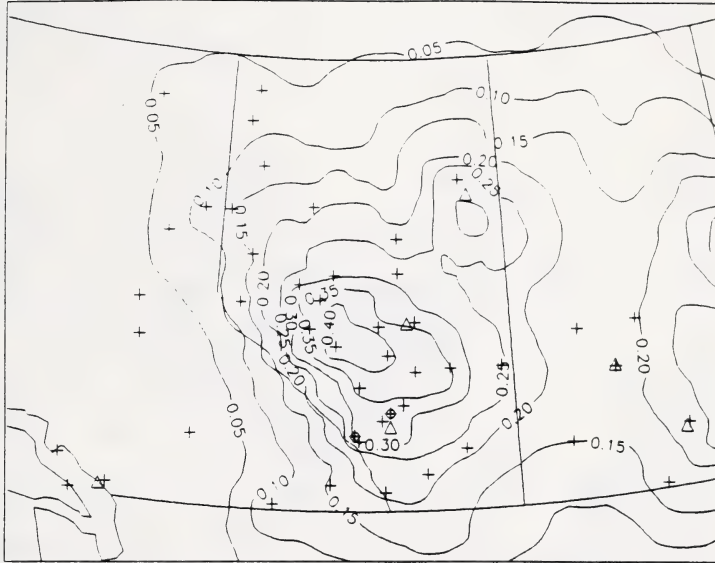
Figure 29. Continued



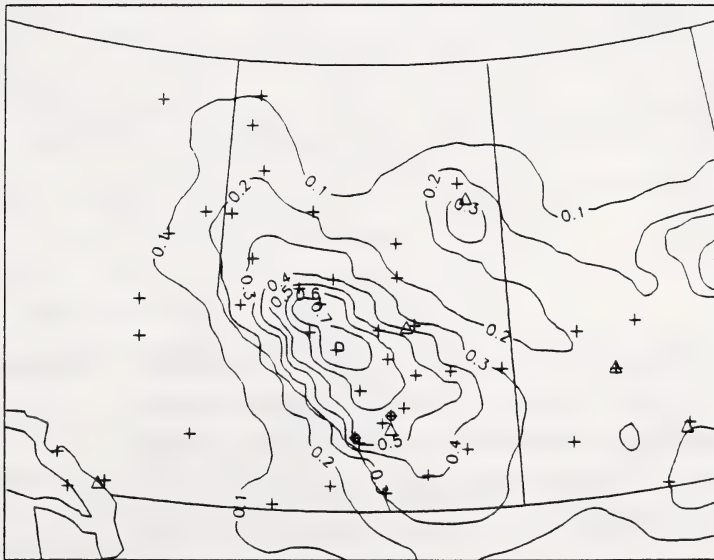


(A)

Figure 30. RELMAP simulated seasonal mean concentration of sulphate ( $\mu\text{g m}^{-3}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +’s denote locations of emission source and  $\Delta$ ’s are major cities.

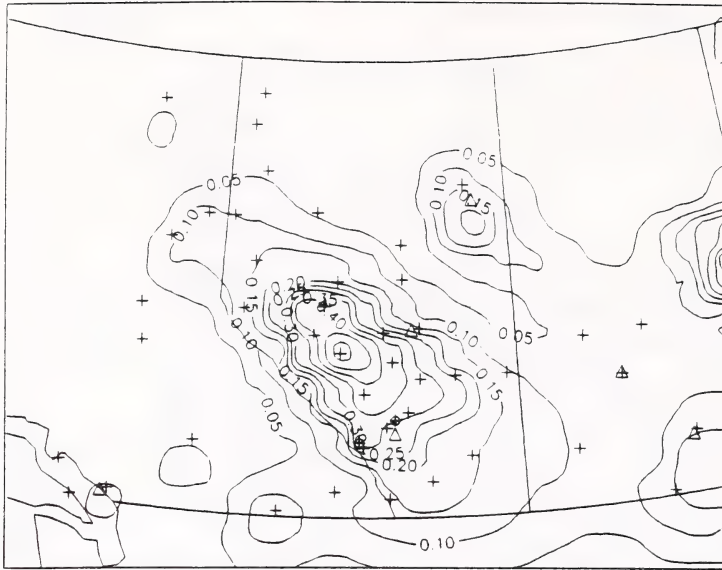


(B)

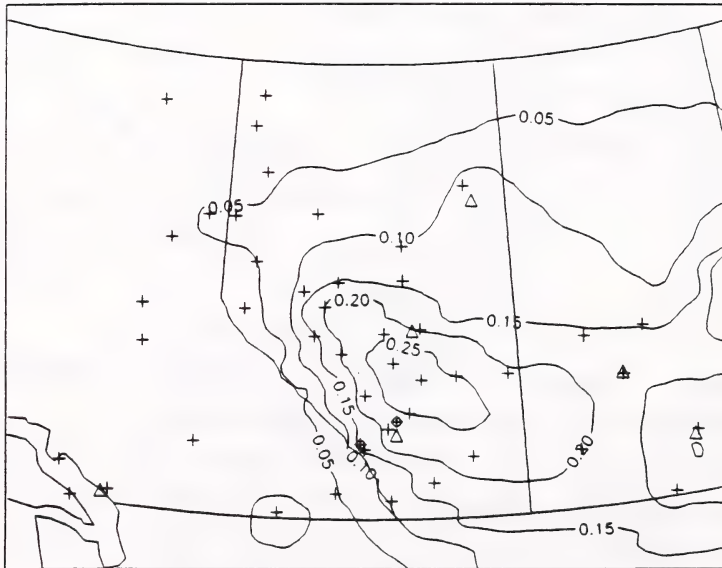


(C)

Figure 30. Continued

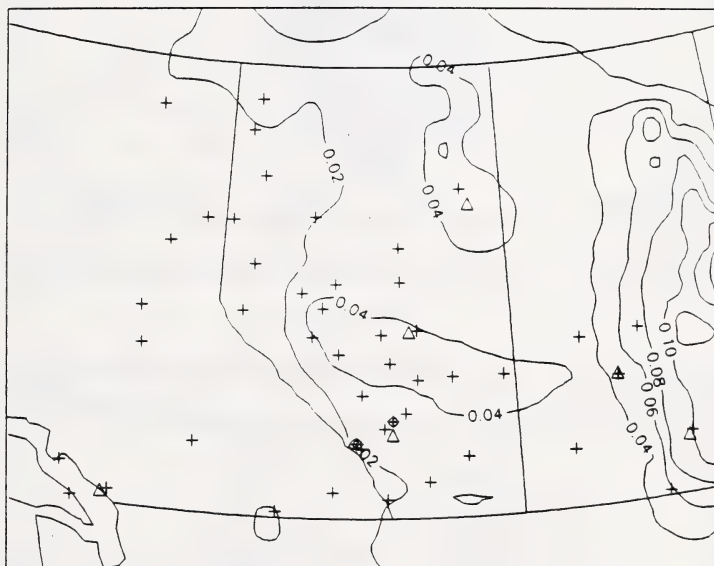


(D)



(E)

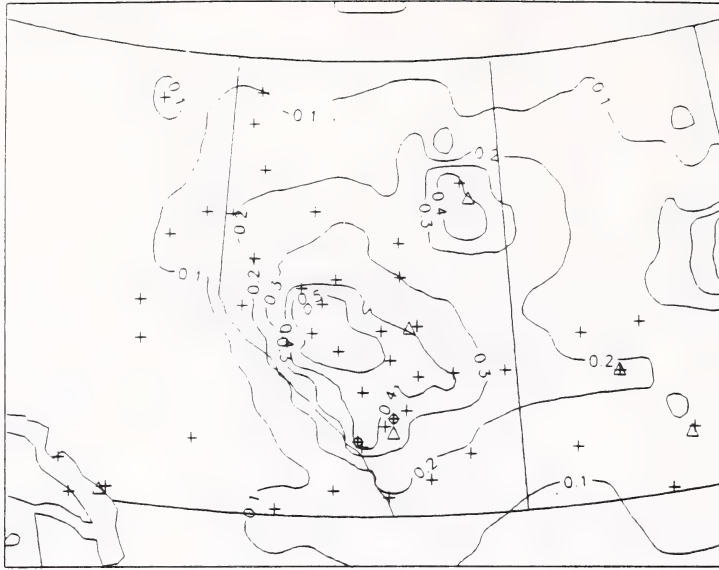
Figure 30. Continued



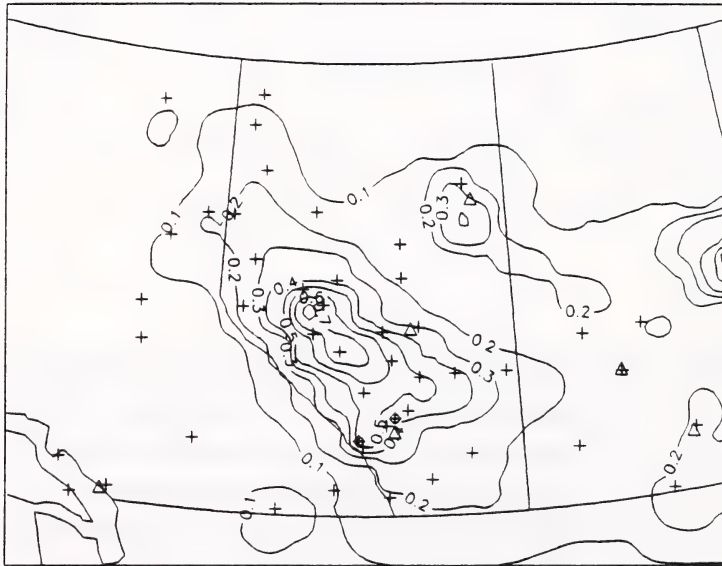
(A)

Figure 31. RELMAP simulated seasonal dry deposition of sulphur dioxide ( $\text{kg ha}^{-1}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +'s denote locations of emission source and  $\Delta$ 's are major cities.



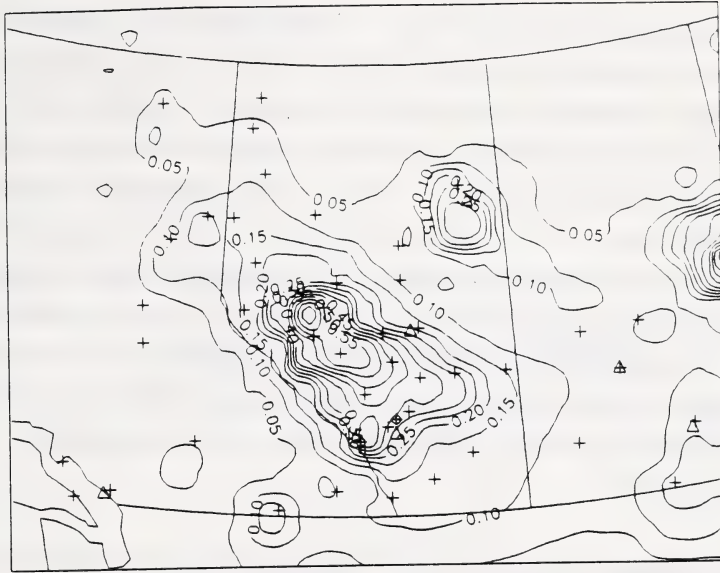


(B)



(C)

Figure 31. Continued



(D)



(E)

Figure 31. Continued

The simulated seasonal  $\text{SO}_4^{2-}$  dry depositions are presented in Figure 32. Except for the summer season, the distributions of  $\text{SO}_4^{2-}$  did not appear to be determined primarily by the location of sources. The influence of downwind transport seemed to be greater. In summer, the transformation rate was high and the dry deposition velocity of  $\text{SO}_4^{2-}$  was appreciable because of the unstable atmosphere. The locations of maximum  $\text{SO}_4^{2-}$  dry depositions could be identified with the emission sources. The simulated summer dry deposition of  $\text{SO}_4^{2-}$  was affected significantly by the change in the wet deposition rate constant. The summer dry deposition of  $\text{SO}_4^{2-}$  obtained from simulation using the default summer wet deposition rate constants was higher by at least a factor of two everywhere in Alberta. This effect was not that considerable in the  $\text{SO}_2$  dry deposition field.

The seasonal  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  wet depositions are shown in Figures 33 and 34. The distribution of seasonal  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  wet depositions depended upon the precipitation pattern and the wet deposition rate. Maximum wet depositions occurred in summer when the rates were high and minimum in winter when the rates were low. The summer  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  wet depositions were higher than those in spring, which in turn were higher than those in autumn. Since that wet deposition rate constants used in these simulations were the same, the wet depositions depended upon the amount of precipitation. Using the default summer wet deposition rate constants in the simulation, the predicted summer  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  wet depositions were increased by factors of about 3 and 1.5 respectively. The distributions were very sporadic, which reflected the pattern of precipitation event in the Prairies.

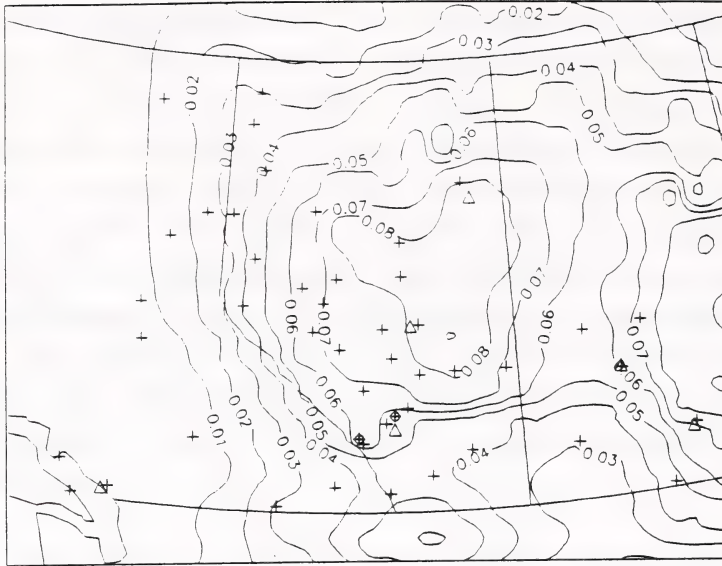
Figure 35 gives the seasonal distributions of total deposition of sulphur. Total deposition of sulphur was highest in summer and lowest in winter. There was about an order of magnitude difference between the total depositions of sulphur in summer and that in winter. The maximum summer total depositions of sulphur calculated by the default summer wet deposition rate constants was higher by a factor of three.

The seasonal distributions of dry/wet ratio of deposition are presented in Figure 36. The seasonal dry/wet ratio varied from mostly dry higher than wet in

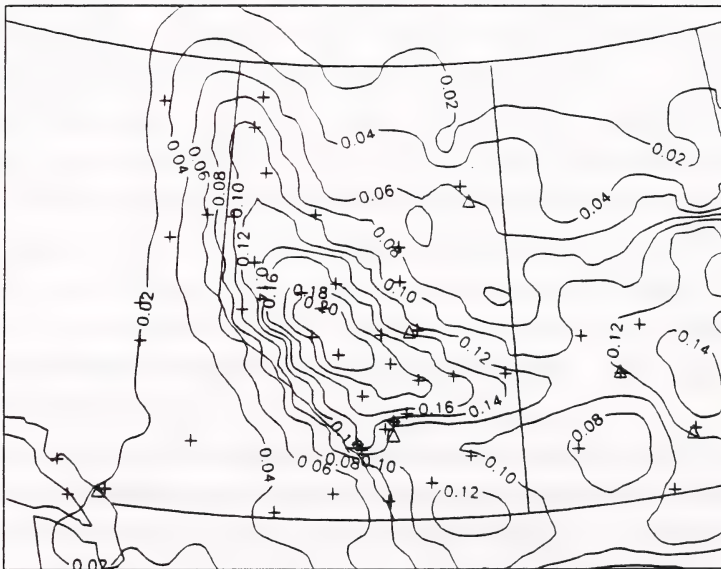


(A)

Figure 32. RELMAP simulated seasonal dry deposition of sulphate ( $\text{kg ha}^{-1}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +'s denote locations of emission source and  $\Delta$ 's are major cities.



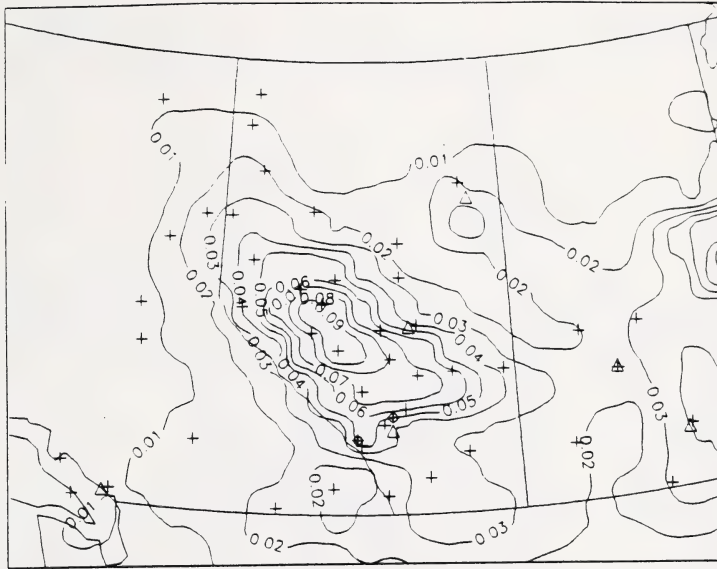
(B)



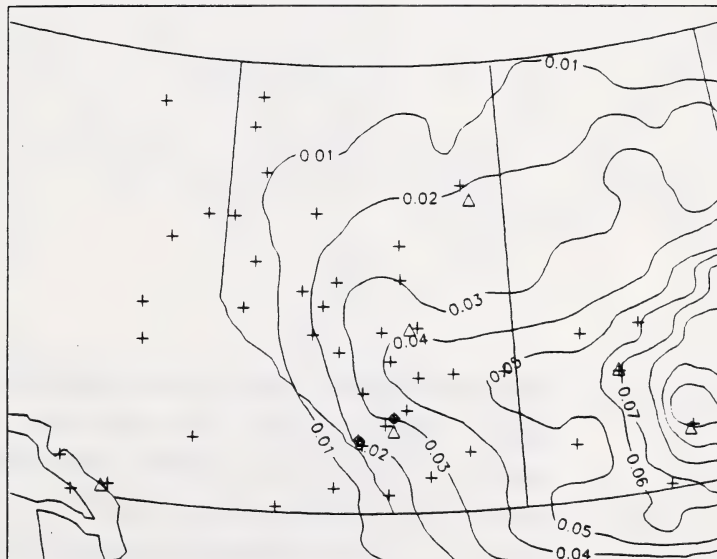
(C)

Figure 32. Continued



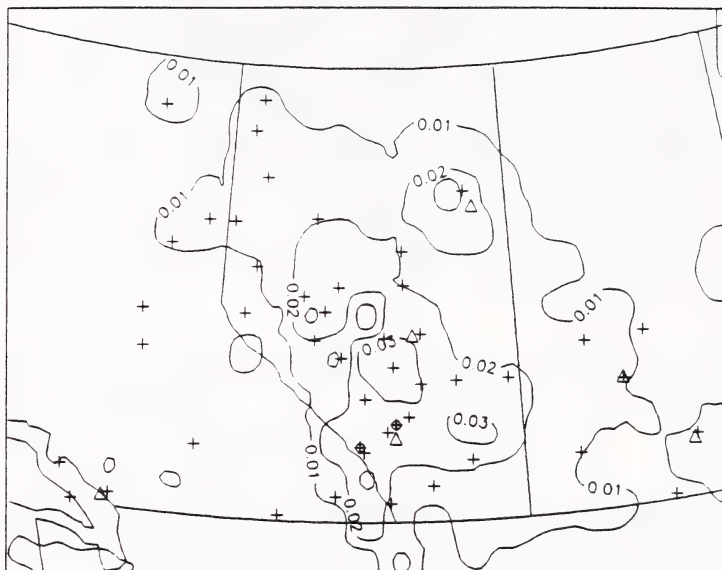


(D)



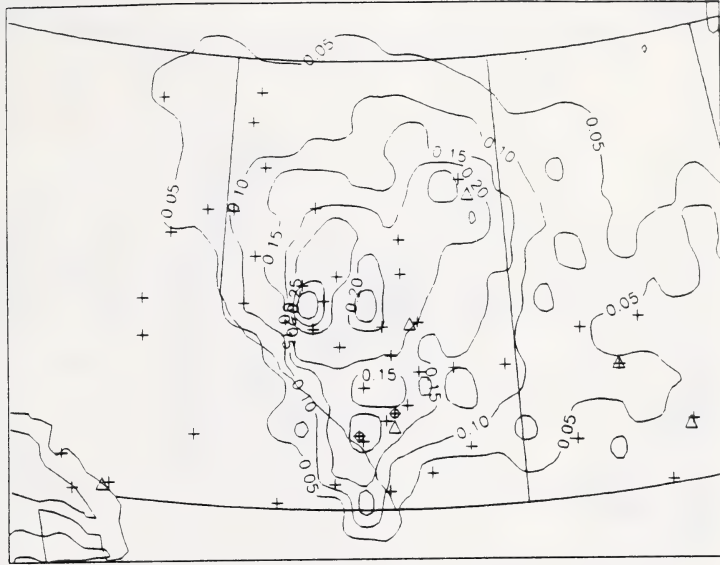
(E)

Figure 32. Continued



(A)

Figure 33. RELMAP simulated seasonal wet deposition of sulphur dioxide ( $\text{kg ha}^{-1}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +’s denote locations of emission source and  $\Delta$ ’s are major cities.



(B)



(C)

Figure 33. Continued

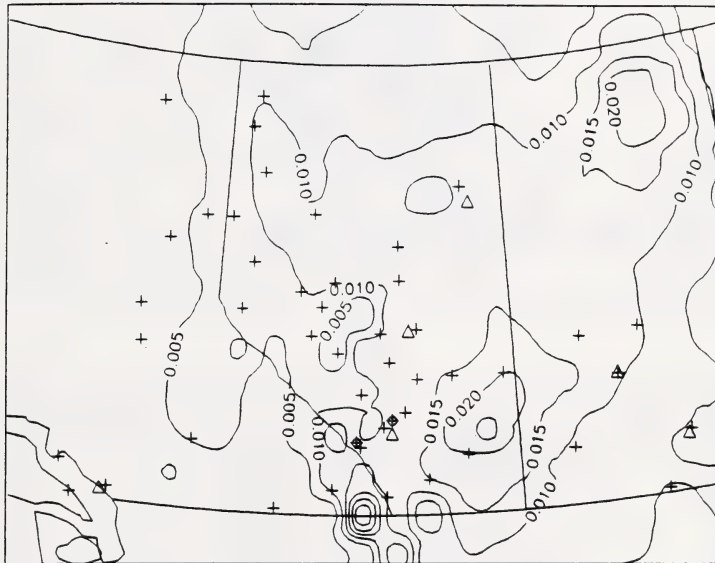


(D)



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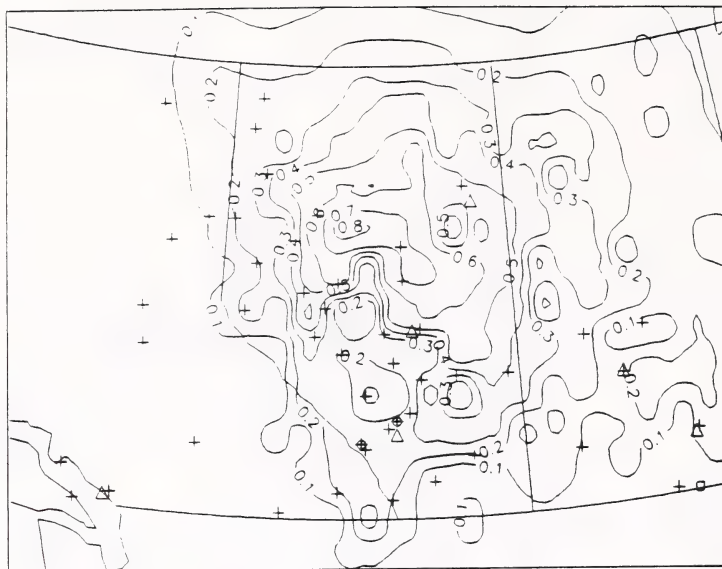
Figure 33. Continued



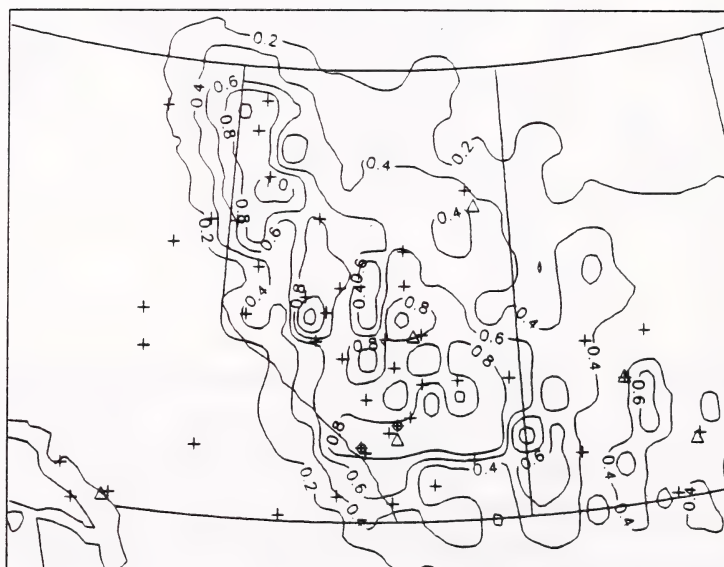
(A)

Figure 34. RELMAP simulated seasonal wet deposition of sulphate ( $\text{kg ha}^{-1}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +'s denote locations of emission source and  $\Delta$ 's are major cities.



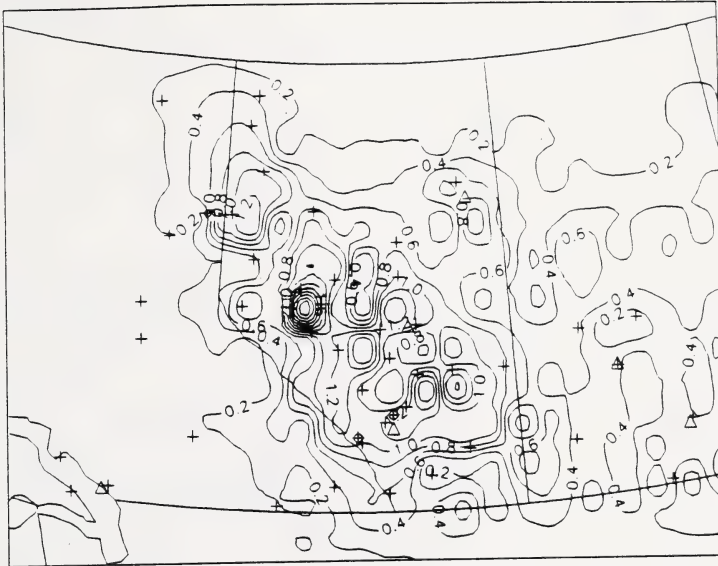


(B)

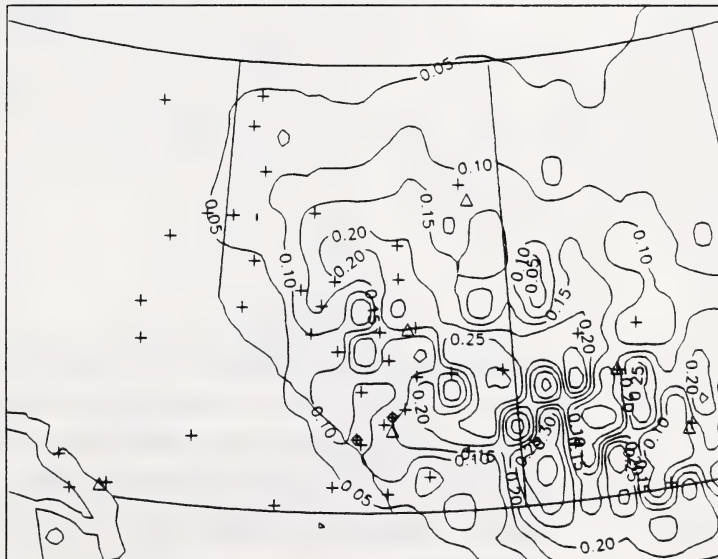


(C)

Figure 34. Continued

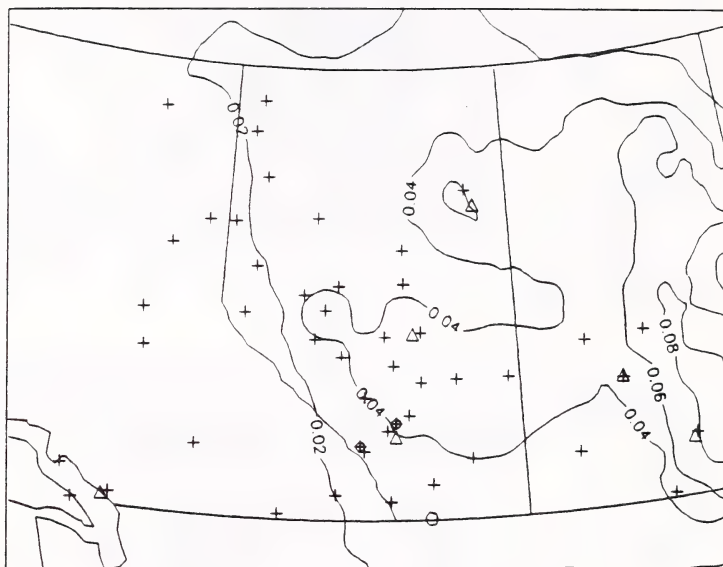


(D)



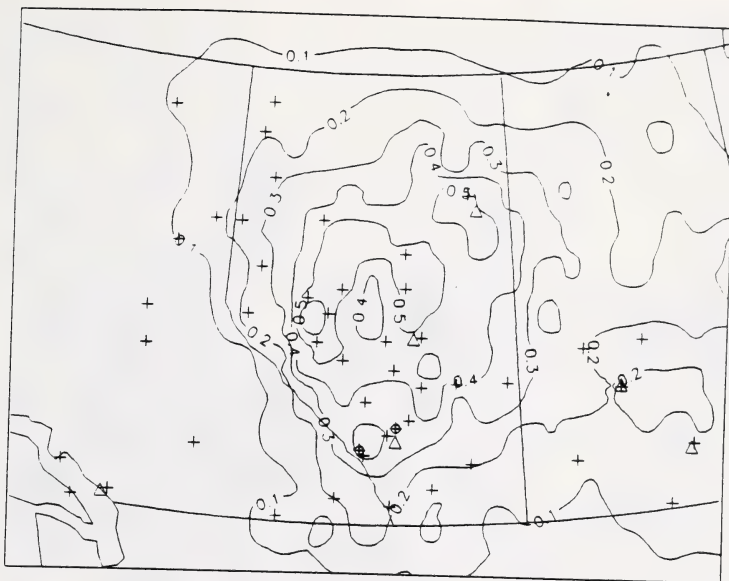
(E)

Figure 34. Continued

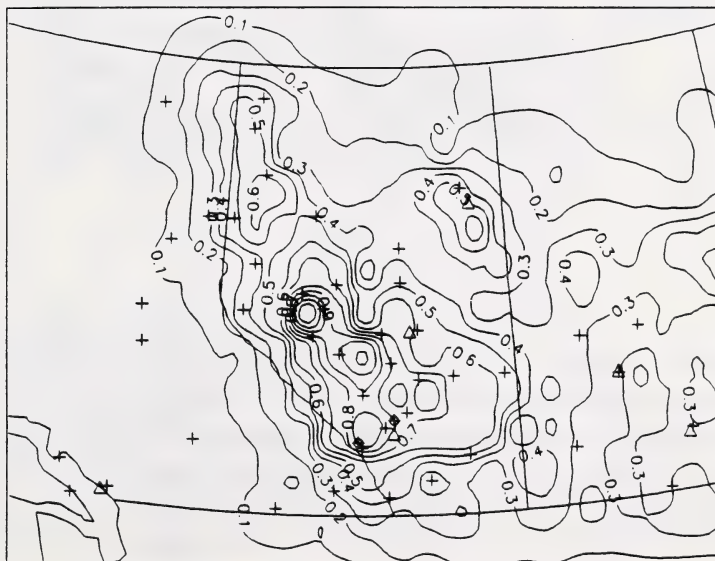


(A)

Figure 35. RELMAP simulated seasonal total deposition of sulphur ( $\text{kg ha}^{-1}$ ) for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +'s denote locations of emission source and  $\Delta$ 's are major cities.

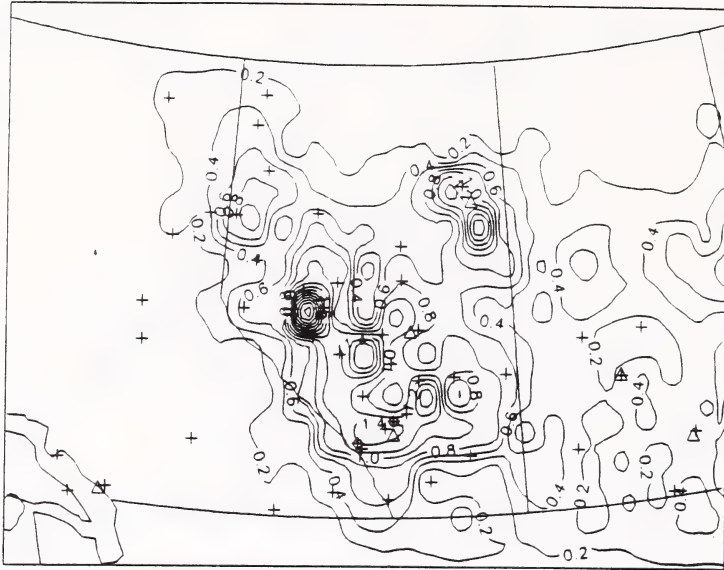


(B)

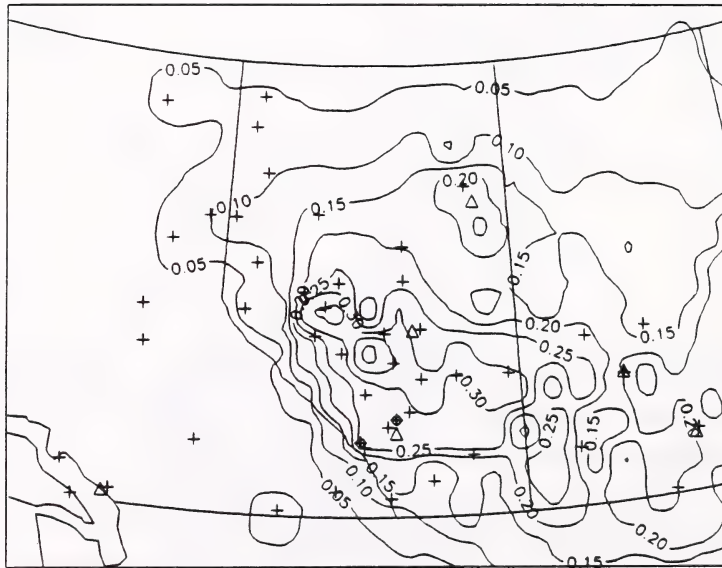


(C)

Figure 35. Continued



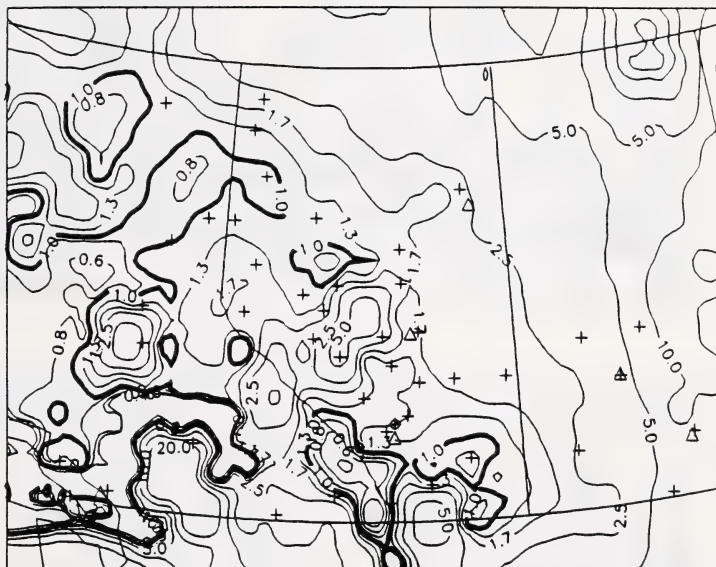
(D)



(E)

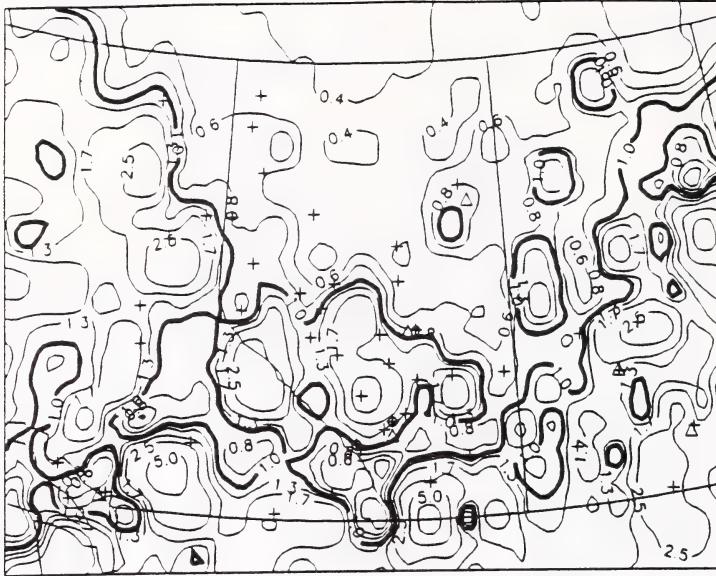
Figure 35. Continued



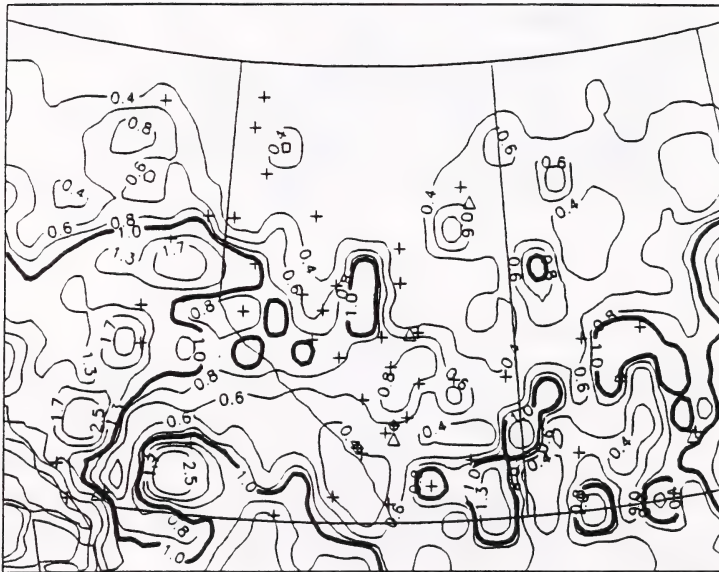


(A)

Figure 36. RELMAP simulated seasonal dry/wet ratio of deposition for (A) winter; (B) spring; (C) summer; (D) summer using default summer wet deposition rate constants; and (E) autumn. +’s denote locations of emission source and Δ’s are major cities.



(B)



(C)

Figure 36. Continued



(D)



(E)

Figure 36. Continued

winter to all dry lower than wet in summer. In spring and fall, dry deposition of sulphur was higher than wet deposition near major emission sources (foothills at central Alberta and Fort McMurray) and at southern Alberta where precipitation was infrequent. Elsewhere, wet deposition was higher than dry deposition in spring and autumn. Using the default summer wet deposition rate constants in the simulation, the predicted summer dry/wet ratio of deposition was mostly less than one, which was very different than the results of the winter, spring and autumn simulations.







## SECTION 2

Assessment of the Acid Rain  
Mountain Mesoscale  
Model (ARM3)



ASSESSMENT OF THE ACID RAIN  
MOUNTAIN MESOSCALE  
MODEL (ARM3)

by

Lawrence Cheng

Environmental Research & Engineering Department  
Alberta Research Council

and

Randy P. Angle

Standards and Approvals Division  
Alberta Environment

for

ACID DEPOSITION PROGRAM  
ALBERTA ENVIRONMENT

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### ABSTRACT

The performance of the ARM3 model has been assessed and compared with simulation results of the RELMAP model. The ARM3 modeling results differed significantly from the observations and from the simulation results of RELMAP. ARM3 predicted that a maximum annual mean ground level SO<sub>2</sub> concentration of 6.0 µg m<sup>-3</sup> occurred near the Whitecourt area while RELMAP indicated a maximum of 1.2 µg m<sup>-3</sup> to the southeast of the source region near Fort McMurray. Considerable computational time and storage were required by the ARM3 simulations. The model is not suitable for impact assessments at large downwind distances. However, for single sources, or for impacts of future economic developments in the foothills areas, ARM3 could be useful. Further testing of ARM3 is recommended.



### ACKNOWLEDGMENTS

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## 1. INTRODUCTION

Long-term deposition of acidic and acid-forming substances can alter the structure and function of aquatic and terrestrial ecosystems. The impacts of acidic deposition on aquatic and terrestrial ecosystems are difficult to predict because the effects are exceedingly complex, subtle and long-term. Furthermore, every ecosystem has a different inherent capacity to resist acidification. A single standard on acidic loadings to preserve environmental integrity is not realistic. A sensible management objective is to balance acidic loading with the sensitivity of a particular ecosystem to acid deposition. The target loadings, which is defined as the maximum level of acidic atmospheric deposition that will not cause any long-term ecological damage and that is practically and politically achievable, is, therefore, adopted as part of the management strategy for controlling acidic deposition in Western and Northern Canada.

The effects of acidic emissions can be determined through epidemiological, field observational, or numerical modelling studies. For regional-scale studies, mathematical modelling is the most cost-effective way of linking emissions to loading under complex meteorological and source conditions. Modelling of the transport, chemical transformation and deposition of acidifying constituents is essential to interpolate or extrapolate monitoring data, because of the lack of sufficient monitoring data to define the level of loadings being experienced by the aquatic and terrestrial ecosystems. Moreover, atmospheric acid deposition modelling is the only method by which projection of effects due to future economic development can be made quantitatively.

Three mesoscale (20-2000km) atmospheric acid deposition models have been compared for their application in northern Alberta and Saskatchewan (Cheng

et al., 1990). The MESOScale Puff (MESOPUFF-2) model is a short term (1 day to 1 month) acid deposition model. The REgional Lagrangian Model of Air Pollution (RELMAP) is a long term (1 month to 1 year) model. The statistical Estimates of Regional Transport and Acid Deposition (SERTAD) is a statistical long-range transport model that assumes steady state and handles the crosswind diffusion separately using a "pollutant rose concept". SERTAD cannot be used in episodic applications.

MESOPUFF-2 (Scire et al., 1984) makes use of Briggs formulation to calculate plume rise. The boundary-layer structure is treated in terms of microphysical parameters that include the surface frictional velocity, mixing height, convective velocity scale, and Monin-Obhukov length. The model uses an integrated form of the puff sampling function that eliminates the problem of insufficient puff overlap commonly encountered with puff superposition models and provides concentrations and amounts of deposition at gridded and non-gridded (discrete) receptors. Therefore, MESOPUFF-2 has been considered the best overall Lagrangian mesoscale deposition model for short-term or episodic simulations (Thomson et al., 1987). The computational requirements of the model depend upon the simulation period, domain area, number of receptors, wind speed and direction, and number of emission sources. It is very costly for long-term simulations with numerous sources.

On the other hand, the pertinent physical and chemical processes in the RELMAP model (Eder et al., 1986) are highly parameterized by using available data and current theories to create a regional model capable of simulating monthly concentrations and depositions of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , and fine and coarse particulate matter. These parameterizations are representative for long-term periods (e.g., one month) and must not be interpreted as being representative for shorter

periods. The model is designed as a regulatory tool and is operable with: (1) a small volume of input data, (2) short data processing and CPU times, and (3) low computer costs.

It has been shown that both models predicted the maximum values of ground level  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations and the accumulative amounts of dry, wet and total depositions to be located close to the source region (Cheng et al., 1990). The simulation results from both models also illustrated that the contribution of wet deposition to sulphur loading to be about the same as that of dry deposition, if not smaller. However, the wet deposition of sulphur predicted by these models did not agree with observations. Possible reasons suggested for such disagreement were limited emission sources, excluding background and lateral boundary flux of pollutants, inappropriate model parameters, lack of weather and precipitation coverage, and difficulties with interpretation of precipitation quality measurements (background and dust contamination).

Judging from the practicability and the physical and chemical processes involved, RELMAP was considered to be the most appropriate model for linking emissions to pollutant loading in Alberta. In addition to the model's ability to simulate monthly, seasonal and annual depositions, a total sulphur budget in the model's domain is generated. The sulphur budget is useful in estimating the distribution of the primary and secondary pollutants.

In a parallel effort, the U. S. National Acid Precipitation Assessment Program (NAPAP) has compared RELMAP with the more comprehensive state-of-the-art REGIONAL Acid Deposition Model, RADM, (NCAR, 1985) and shown that these models produced consistent annual wet and total sulphur deposition fields for eastern Northern America, though the maximum dry deposition



value predicted by RELMAP is almost twice that calculated by RADM (NAPAP, 1989). The discrepancy in maximum dry deposition value may be attributed to the Lagrangian setting in RELMAP and the Eulerian setting in RADM.

RELMAP does not take into account of the topographical effects on transport and deposition of acidic air pollutants. The topographical influences may be significant in simulating acidic loadings from a single point source in mountainous regions. For such applications as projection of impacts due to future economics development in complex terrain, modification to include an algorithm to account for the complex airflow patterns over the mountainous area is required for RELMAP, or another suitable model is employed.

The Acid Rain Mesoscale Model (ARM3) is developed for the western United States in the Rocky Mountain region. The ARM3 consists of two main components: a mesoscale meteorological model and a Lagrangian acid deposition/air quality model. The mesoscale meteorological model contains a diagnostic wind model that accounts for the kinematic, deflection, and thermal effects that alter the flow fields due to complex terrain. The Lagrangian acid deposition/air quality model contains several modules that have been adopted from other models; some components have several options. The model has not undergone any rigorous operational testing, sensitivity analyses, or validation studies. The ARM3 model is designed to be highly modular so that when new modules describing atmospheric processes become available they can be easily integrated into the model.

The objective of this study is to apply the ARM3 to northern Alberta and Saskatchewan, the same region as in the earlier RELMAP and MESOPUFF-2 comparison study, and estimate deposition patterns resulting from the oil sands



operation. Terrain data within the modelling domain, together with data (1985 meteorological data and emissions from oil sands extraction plants) employed in the RELMAP and MESOPUFF-2 comparison study are used. The simulation results are compared with those produced by the RELMAP, and with observations. The performance and operating characteristics of the ARM3 are evaluated as practical mesoscale deposition model with respect to their prediction capability for northern Alberta and Saskatchewan.

Following this brief introduction, an overview of the data base and a brief description of Acid Rain Mountain Mesoscale Model will be given in section 2. Section 3 presents the simulation results. A general discussion of the simulation results is given in section 4. Section 5 summarizes the findings and presents the recommendations.

## 2. DATA BASE AND THE ACID RAIN MOUNTAIN MESOSCALE MODEL (ARM3)

### 2.1 DATA BASE

The area of study is the region in northern Alberta and Saskatchewan that may be significantly affected by the emissions from the Athabasca Oil Sands extraction plants. It extends from the east of the Saskatchewan-Manitoba border to the eastern foothills of the Canadian Rockies in an east-west direction, and crossing the Northwest Territories border to the central Alberta and Saskatchewan in a north-south direction. Figure 1 gives the location of the study area. Since most of the input data used here are exactly the same as those compiled for the MESOPUFF-2 and RELMAP comparison study, only a brief description of the data base will be given here.

The variability of surface and atmospheric conditions in space and time can cause significant variations in dry deposition rates. The land use data required by ARM3 to calculate the dry deposition rates were extracted from the data bank for Canada.

Routine surface and upper-air meteorological observations are required to generate gridded fields of meteorological variables for the ARM3 modelling domain with updating interval selected by the user. The gridded meteorological variables are: several vertical levels of wind fields, mixing heights, surface pressure, surface temperature, temperature lapse rates below and above the mixing height, surface dew point, dew point lapse rates below and above the mixing height, stability, Monin-Obukhov length, friction velocity, convective velocity and total opaque cloud cover. Thus, hourly surface observations of cloud cover, ceiling height,

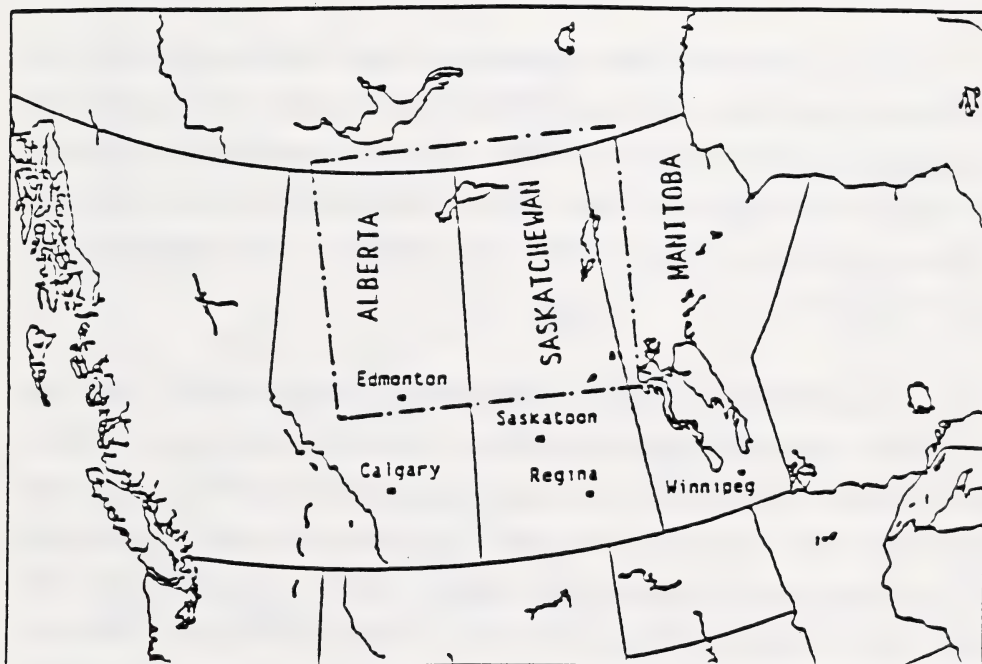


Figure 1. Location of the study area.

precipitation amount and type, wind speed, wind direction, surface pressure, temperature, and dew point temperature were extracted from archived 1985 weather data. Surface meteorological stations operated by the Atmospheric Environment Service, which provide hourly measurements in a 24-h operation mode, were used. The locations of these surface stations are shown in Figure 2.

Routine rawinsonde data of pressure, height, temperature, dew point temperature, wind speed, and wind direction from the surface to a pressure level specified by the user are required by ARM3. Only three Atmospheric Environment Service upper air stations are located within the study area: Fort Smith, Northwest Territories; Edmonton, Alberta; and The Pas, Manitoba. Their locations are also shown in Figure 2.

Although ARM3 can model emission of  $\text{SO}_2$ , sulphate, NO,  $\text{NO}_2$ , nitric acid and nitrates, and particulates from both point and area sources, only the primary point sources of  $\text{SO}_2$  within the study area were considered, namely, the Syncrude and Suncor stacks. For each point source, the emission rate, height and diameter and exit velocity and temperature are required. Monthly emissions of the two plants were provided by Alberta Environment. There are a number of stacks at each oil sands extraction plant: powerhouse/boiler, flare, and sour water stripper. In addition, Suncor has a stack for the incinerator. In general, the powerhouse stack emits more than 70% of the total  $\text{SO}_2$  emission produced by any particular company. In order to save on computation time required for model runs, it was considered that the total emission of each plant emitted through the powerhouse stack in all simulations.

Wet deposition is the sole available measurement for acid deposition model evaluation in northern Alberta and Saskatchewan. Various agencies have

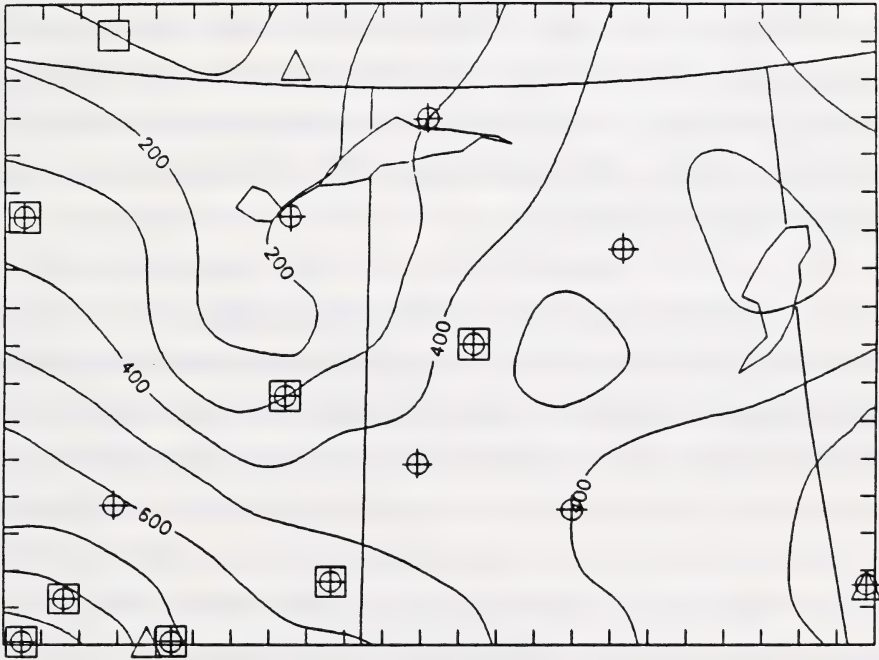


Figure 2. Smoothed terrain elevation (m) of the study area. Locations of surface ( $\square$ ); upper-air ( $\Delta$ ); and precipitation quality monitoring stations ( $\oplus$ ) are also given.



collected rainfall and snowfall samples and performed subsequent chemical analysis in the study area since 1976. The Alberta Precipitation Quality Monitoring Program maintains a number of stations throughout Alberta which provide monthly observations. Seven of these stations were located in the area of interest during 1985. CAPMoN (Canadian Air and Precipitation Monitoring Network) is set up by the Atmospheric Environment Service and provides daily precipitation analysis measurements. However, Cree Lake is the only station in the CAPMoN network within the study area. The locations of these stations are given in Figure 2 also. These measurements are not designed for model evaluation and data were missing at some at some stations.

The ARM3 requires certain terrain statistics averaged over the grid cells of the modelling domain. The 1-km average terrain data, which were generated by a digital elevation model using oil and gas drilling log data and digitized data from elevation maps of the study area, were converted into gridded arrays of cell average terrain height in metres above sea level and terrain roughness values in the model coordinates. The use of too large a mesoscale modelling domain grid cell size may smooth and obscure important terrain feature. Figure 2 displays terrain elevation contours for the present study. Because of the 50 km grid spacing used in this study, details of the terrain features were highly smoothed and, possibly, some important ones were lost.

## 2.2 MODEL DESCRIPTION

The Acid Rain Mountain Mesoscale Model (ARM3) has two main components: a mesoscale meteorological model and an acid deposition/air quality simulation model. The model consists of six interrelated Fortran 77 programs. Only a brief description of the model is given in this report. The reader can consult

the user's guide for a concise summary of the basic model equations (Morris et al. 1988).

The ARM3 is an extension and improvement of the MELSAR model developed by the Pacific Northwest Laboratory for the U. S. Environmental Protection Agency (Alline and Whiteman 1985). Supplied with the ARM3 modelling package is enough topographic, geographic, and meteorological data to carry out an impact assessment for source and receptors within a master modelling domain for the calendar year 1981. This master grid has an origin at (400,4050) UTM zone 12 and extends 750 by 950 km in the x and y directions. The ARM3 can be extended to other regions outside the master modelling domain as in this study, but the user must supply the topographic and meteorological data required. To model time periods other than 1981, users must also supply their own surface and upper-air meteorological and precipitation data. In this study, the model's domain extended 1200 and 900 km in the x and y directions, with 432 grid cells and 50 km grid interval.

The ARM3 is designed to calculate the impacts from emission sources for one year by simulating each month separately and by stepping through each month using time steps of about 1-hour. This allows for smaller input and output files and consequently easier file management.

Wind fields are generated by the ARM3 for the user-selected mesoscale modelling domain at several heights above ground level called "gamma surfaces", which are parallel to the terrain at all time. The heights of these gamma surfaces are specified by the user.

The six main Fortran programs that make up the ARM3 are PRELND,

PRETER, PRECIP, METDWM, CONDEP, and PSTPRC. PRELND is the land use preprocessor. This program uses data from the Geographic Information System (GIS) land use data base and creates gridded fields of surface roughness and fractional land cover for the user-selected mesoscale modelling domain. PRETER is the terrain preprocessor. This program calculated the average terrain heights and terrain roughness values for the mesoscale modelling domain and grid spacing defined by the user. PRECIP is the precipitation preprocessor. This program uses the 24-hour and hourly rainfall data to generate precipitation fields on the user-specified grid and at the user-specified update interval. METDWM is the mesoscale meteorological model. The model uses the data supplied by the preprocessors and the surface and upper-air meteorological observations to create several levels of gridded wind fields and gridded fields of mixing heights, temperatures, temperature lapse rates, stability, and other meteorological variables. CONDEP calculates hourly concentrations and deposition amounts from user-specified sources. The CONDEP program can be run for many different sources or source configurations using the same meteorological data from the preprocessors and the meteorological model. PSTPRC is the postprocessor. This program creates tables of maximum concentrations and cumulative deposition amounts from the concentration and deposition data created by CONDEP.

Modelling of wet deposition requires estimates of precipitation at each grid cell of the modelling region. Spatial extrapolation or interpolation of precipitation represents a special challenge over complex terrain. Precipitation often occurs as the result of terrain-forced lifting of air masses above the point where condensation takes place. After air masses pass over such terrain obstacles, there is no moisture for precipitation on the lee side of the mountain. As a result, there is often augmented precipitation on the windward side of ridges, and rain shadows (minima) in the lee of the ridges. Terrain height and slope are obvious factors in



determining how much precipitation will fall. In ARM3, contributions of precipitation due to terrain effects are added to precipitation estimates obtained by spatial interpolation of observed data. The interpolation scheme for the precipitation data uses both hourly and 24-hour precipitation data and accounts for orographic effects on precipitation. These orographic adjustments in the precipitation interpolation procedure were obtained by analyzing a year's worth of 24-hour precipitation data from the Rocky Mountain region.

A diagnostic wind model is used to generate gridded fields of the horizontal and vertical wind components at several user-specified vertical levels at a specified time. Generation of the wind field is a two step procedure. Step 1 is based on the approach as described by Liu and Yocke (1980). A domain-mean wind is adjusted for the kinematic effects of terrain, thermodynamically generated slop flows, and blocking effects based on a set of gross parameterization of these effects. Step 1 produces a spatially varying gridded field of  $u$  and  $v$  at each vertical level. Step 2 involves the addition of observational information to the step 1 wind field. An objective analysis scheme and a three-dimensional divergence minimization procedure are used. The scheme is designed so that the observations are weighted relatively heavily in subregions where they are deemed representative of the mesoscale airflow, whereas step 1 wind values are weighted heavily in subregions in which observations are unrepresentative or unavailable.

The gridded mixing heights are computed for each hour from surface weather and upper-air observations. The hourly mixing height at a grid point is the maximum of a convective mixing height or a mechanical mixing height. Stability classification, friction velocity, convective velocity, Monin-Obukhov length are computed for each grid cell for each hour using surface observations.

The acid deposition/air quality simulation model component of ARM3 is a Lagrangian puff model contained in the program CONDEP. In the model pollutant concentration distributions are described in a Gaussian fashion about a puff's centre of mass. The Gaussian puffs are assumed to be circulate, and their horizontal extent is prescribed through the horizontal dispersion parameter. The vertical distribution of the puff may be Gaussian, defined by the vertical dispersion parameter, or it may be uniformly mixed and limited by the mixing height. The user has an option of always assuming that the puffs are uniformly mixed in the vertical. There are three options for computing horizontal and vertical dispersion parameters: Irwin's general formulae (Irwin 1983), MacCready's parameterization based on the terrain roughness (MacCready et al. 1974), or the dispersion formulae in the MESOPUFF-2 model (Scire et al. 1984).

The calculation of dry deposition is based upon the resistance approach, using the grid cell averaging techniques employed in the comprehensive RADM model (Walcek et al. 1986). The deposition velocity, defined as the ratio of the vertical pollutant flux at a reference height to the concentration at that height, is the inverse of a sum of the resistances to pollutant transfer through the atmosphere to the surface. The aerodynamic resistance ( $r_a$ ) and the quasi-laminar sublayer resistance ( $r_b$ ) apply to both gases and particles. The surface resistance ( $r_s$ ) is applicable only to gaseous species. If the species of interest is a particle, the quasi-laminar layer resistance and a virtual resistance ( $r_a r_b V_g$ ) are combined in series with the aerodynamic resistance. The gravitation settling resistance ( $1/V_g$ ) is treated as a parallel resistance. As given in Table 1, the surface resistances for  $\text{SO}_2$  have seasonal and diurnal variations, and also vary if the surface is wet.

The ARM3 contains the MESOPUFF-2 wet scavenging algorithm (Scire et al. 1985), i.e., a scavenging coefficient approach is used to calculate the wet



Table 1. SO<sub>2</sub> surface resistances (s m<sup>-1</sup>).

LAND USE	SEASON	INSOLATION (Watts m <sup>-2</sup> )			NIGHT	WETTED
		>400	200-400	0-200		
Urban	spring	1000	1000	1000	1000	1000
	summer	1000	1000	1000	1000	0
	early fall	1000	1000	1000	1000	1000
	late fall	1000	1000	1000	1000	1000
	winter	200	200	200	200	200
Agriculture	spring	50	60	75	100	0
	summer	70	120	200	500	0
	early fall	500	500	500	500	100
	late fall	50	50	50	50	50
	winter	100	100	100	100	100
Range	spring	100	140	200	400	0
	summer	100	140	200	500	0
	early fall	500	500	500	500	100
	late fall	500	500	500	500	100
	winter	100	100	100	100	100
Deciduous forest	spring	100	200	400	1000	0
	summer	60	130	300	1000	0
	early fall	1000	1000	1000	1000	500
	late fall	1000	1000	1000	1000	500
	winter	1000	1000	1000	1000	1000
Coniferous forest	spring	150	240	400	1000	0
	summer	150	240	400	1000	0
	early fall	800	800	800	800	100
	late fall	800	800	1000	1000	100
	winter	500	500	500	500	500
Forested swamp	spring	100	200	400	1000	0
	summer	70	140	300	1000	0
	early fall	800	800	800	800	300
	late fall	800	800	1000	1000	300
	winter	800	800	800	800	800
Water	spring	0	0	0	0	0
	summer	0	0	0	0	0
	early fall	0	0	0	0	0
	late fall	0	0	0	0	0
	winter	0	0	0	0	0
Swamp	spring	50	60	75	100	0
	summer	50	60	75	100	0
	early fall	100	100	100	100	75
	late fall	100	100	100	100	75
	winter	100	100	100	100	100
Agriculture-range mixture	spring	75	100	150	250	0
	summer	100	140	200	500	0
	early fall	500	500	500	500	100
	late fall	200	200	200	200	100
	winter	100	100	100	100	100

deposition. This approach assumes that the loss of pollutant mass over one time step,  $\Delta t$  (s), due to a precipitation rate,  $R$  (mm/h), is expressed as follows:

$$Q(t+\Delta t) = Q(t) \exp(-\Lambda \Delta t) \quad (2)$$

where  $Q(t)$  and  $Q(t+\Delta t)$  represent the mass of the pollutant at the beginning and end of the time step, and  $\Lambda$  ( $s^{-1}$ ) is the scavenging ratio expressed as  $\Lambda = \lambda(R/R_1)$ . Here  $R_1$  is a reference rainfall rate (1 mm/h), and  $\lambda$  is the scavenging coefficient ( $s^{-1}$ ) whose value depends on the species and whether the precipitation is liquid or frozen. The species-dependent scavenging coefficients are listed in Table 2. The precipitation rate  $R$  used in the ARM3 is the precipitation rate obtained from the precipitation preprocessor, PRECIP, in the grid cell containing the centroid of the Lagrangian puff.

Table 2. Default values of the scavenging coefficient  $\lambda$  ( $s^{-1}$ ).

Pollutant	Liquid Precipitation	Frozen Precipitation
SO <sub>2</sub>	$3 \times 10^{-5}$	0.0
SO <sub>4</sub> <sup>2-</sup>	$1 \times 10^{-4}$	$3 \times 10^{-5}$

There are three options for calculating chemical transformation in ARM3: no chemical transformation (inert), RIVAD condensed pseudo-first-order chemistry, or MESOPUFF-2 empirical pseudo-first-order chemistry. The RIVAD and MESOPUFF-2 chemical mechanisms are both called pseudo-first-order chemical mechanisms because any nonlinearities in the chemical transformation rates are

based on conditions that can be described within the Lagrangian puff. The RIVAD chemical mechanism is similar to that used in the U. S. Environmental Protection Agency's plume visibility model PLUVUE (Johnson et al. 1980), but is modified slightly to account for the effect of clouds. The RIVAD mechanism estimates the concentration of hydroxyl radical, the primary oxidizer of  $\text{SO}_2$  and  $\text{NO}_2$  in the gas-phase. The RIVAD chemistry algorithms assume low background concentrations of VOC's, and thus are appropriate for regions with low background levels of reactive compounds, such as the relatively clean nonurban areas. Transformation rate expressions were developed for use in MESOPUFF-2 chemical mechanism by statistically analyzing hourly transformation rates produced by a photochemical box model. The model employed the RHC/ $\text{NO}_x$ / $\text{SO}_x$  chemical mechanism developed by Atkinson and co-workers (Atkinson et al. 1982). Plume  $\text{SO}_x$ / $\text{NO}_x$  dispersing into background air containing ozone and reactive hydrocarbons (RHC) was simulated over a wide range of conditions representing different solar radiation intensities, temperatures, dispersion conditions, background ozone and RHC levels, plume  $\text{NO}_x$  concentrations, and emission times. An evaluation of these two mechanisms by the ARM3 model developer indicated that the RIVAD chemistry module seemed to produce more realistic responses to changes in environmental conditions and concentrations than the MESOPUFF-2 module, and thus is recommended in the model.

### 3. SIMULATION RESULTS

Monthly simulations were conducted using ARM3 to simulate monthly averaged ground level concentrations, and monthly wet and dry depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  in the northern Alberta and Saskatchewan region. Only emissions from the oil sands extraction plants were included. Seasonal and annual averaged concentrations and the amounts dry, wet and total depositions for the respective periods were generated from the monthly values. The seasonal results are presented in Appendix 7.1.

The distribution of the simulated annual mean ground level  $\text{SO}_2$  concentration is given in Figure 3. Locations of the emission sources and precipitation quality monitoring stations are also shown. Typical values of  $\text{SO}_2$  concentration ranged from  $<0.1 \mu\text{g m}^{-3}$  to  $>6.0 \mu\text{g m}^{-3}$  within the modelling domain. The maximum annual averaged  $\text{SO}_2$  concentration was located near Whitecourt. The distribution of the concentrations appears to be strongly affected by the topography. Northeast winds towards the mountains, generated by the diagnostic wind model due to the kinematic effects of terrain and thermodynamically created slope flow, transported the pollutant in that direction. The blocking effects of the mountain ranges decelerated the flow and produced a maximum concentration ahead of the highest elevation point within the modelling domain. The isopleths of concentration protruded to the northeast and southeast of the emission sources as well, suggesting significant advection to those directions.

The distribution of the annual averaged sulphate concentration is shown in Figure 4. As it is pointed out earlier, because dispersion and transport of  $\text{SO}_2$  must take place during the production of sulphate, the pattern of sulphate concentration is very similar to that of the  $\text{SO}_2$ . Maximum sulphate annual mean



Figure 3. Simulated annual average SO<sub>2</sub> concentration ( $\mu\text{g m}^{-3}$ ).  $\square$ s denote monitoring stations and +s are emission sources.



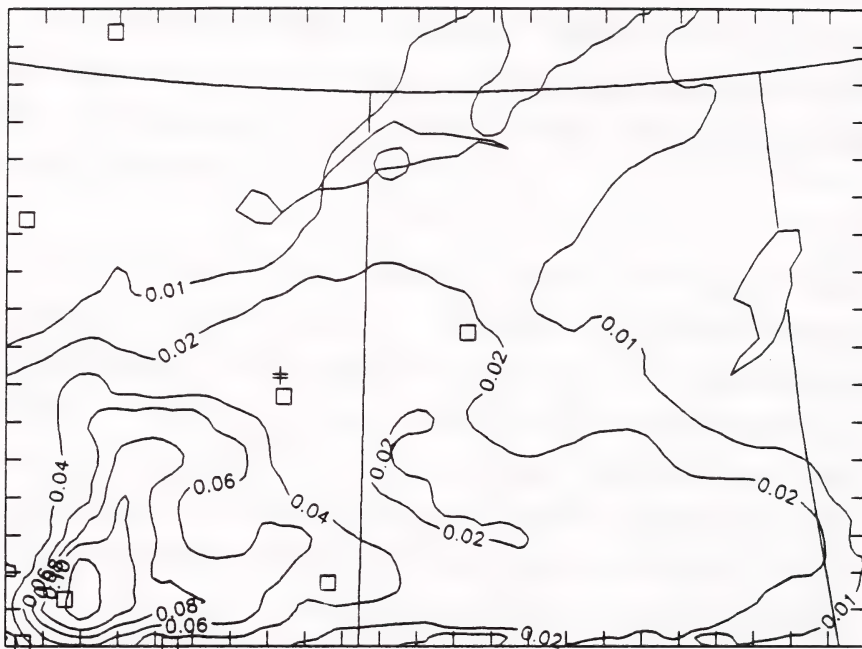


Figure 4. Simulated annual  $\text{SO}_4^{2-}$  concentration ( $\mu\text{g m}^{-3}$ ).  $\square$ s denote monitoring stations and +s are emission sources.

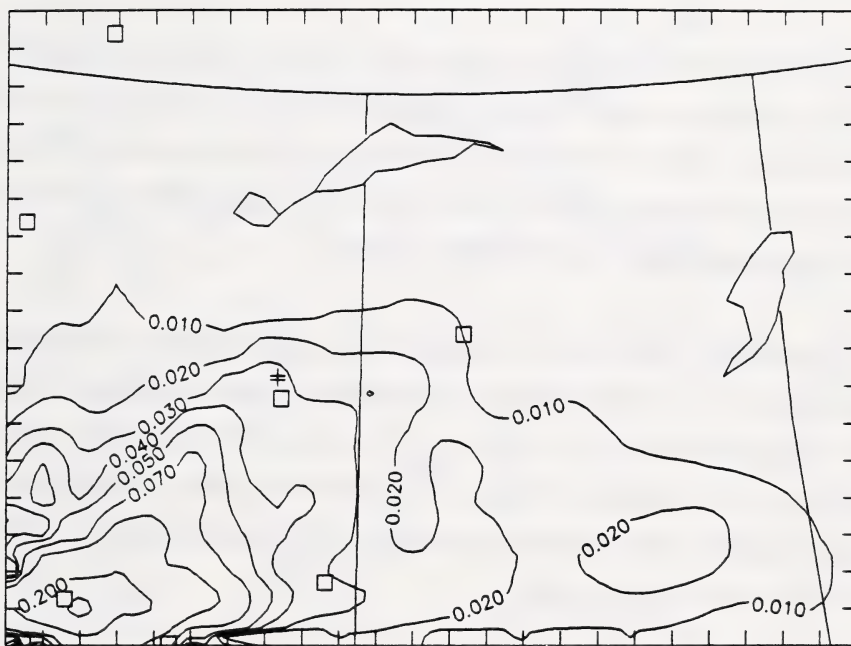


Figure 5. Simulated annual dry deposition of sulphur ( $\text{kg ha}^{-1}$ ).  $\square$ 's denote monitoring stations and +'s are emission sources.

concentration of value  $>0.14 \mu\text{g m}^{-3}$  was located near Whitecourt, slightly to the north of the maximum  $\text{SO}_2$  concentration location. The northeast and southeast protrusions of the sulphate concentration isopleths were more pronounced than those of the  $\text{SO}_2$  concentration contours. This indicates that the transport of  $\text{SO}_2$  was very rapid, and thus the production of sulphate occurred further downstream.

The distribution of annual dry deposition of sulphur is given in Figure 5. The annual dry deposition pattern had an appearance similar to the  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations. Maximum dry deposition of  $0.4 \text{ g ha}^{-1}$  occurred near Whitecourt. Aside from the Whitecourt area, a local maximum dry deposition of  $0.02 \text{ kg ha}^{-1}$  existed to the southeast of the emission sources.

The pattern of annual wet deposition of sulphur dioxide and sulphate is shown in Figure 6. The distribution of wet depositions was very patchy. Simulated values ranged from  $0.0$  to  $0.5 \text{ kg ha}^{-1}$ . The maximum deposition was near Whitecourt, in the foothills of Alberta. The predicted pattern indicates that the precipitation events associated with the uplifting of air masses were very important on the wet removal of pollutants.

Figure 7 gives the annual total deposition of sulphur. The distribution of annual total deposition of sulphur resembled that of the dry deposition and the concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , showing the dominance of dry deposition over its wet counterpart, in most part of the modelling domain. Deposition of sulphur occurred everywhere within the modelling domain. Maximum total deposition of sulphur of  $1.0 \text{ kg ha}^{-1}$  was located near Whitecourt. The isopleths of deposition also protruded significantly to the northeast and southeast of the emission sources.

The summer seasonal and annual observed and ARM3 predicted wet

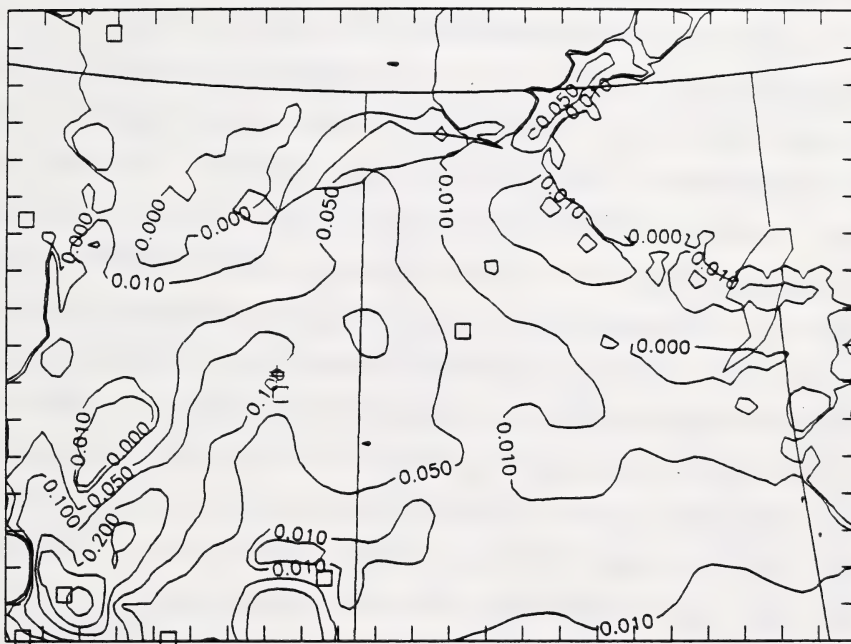


Figure 6. Simulated annual wet deposition of sulphur ( $\text{kg ha}^{-1}$ ). □s denote monitoring stations and +'s are emission sources.

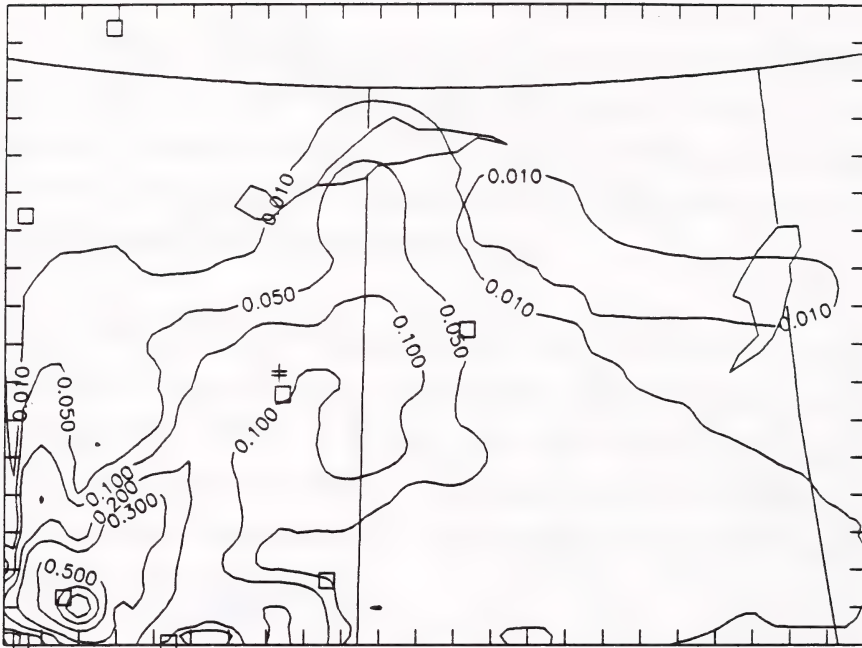


Figure 7. Simulated annual total deposition of sulphur ( $\text{kg ha}^{-1}$ ).  $\square$ 's denote monitoring stations and +'s are emission sources.



deposition of total sulphur at the precipitation quality monitoring stations are summarized in Tables 3 and 4. Included in the tables are those available values predicted by MESOPUFF-2, RELMAP and SERTAD in the mesoscale acid deposition models comparison study (Cheng et al., 1990). The ARM3 predictions at those stations (Fort McMurray and Cree Lake) near or downwind from (east of) the source region were lower than those predicted by the other models. However, upwind from (west of) the emission sources the ARM3 simulated wet depositions were considerably higher, especially at Whitecourt where very high wet deposition was measured. Obviously, the ARM3 predictions underestimated the wet deposition of sulphur at the precipitation quality monitoring stations. The ARM3 model performance was evaluated based on the statistical aspects of the comparison of the observed and predicted wet deposition values. The evaluation measures used were mainly based on those described by Fox (1981), and Willmott et al. (1985). These measures showed that the model performed poorly when compared with observations. The portions of systematic differences were large. Interestingly, the correlation coefficients were relatively high, 0.60 and 0.89, respectively, for the summer seasonal and annual wet depositions. Possible reasons for the disagreement between the prediction and observation are those discussed in Cheng et al. (1990): limited emission sources, excluding background and lateral boundary flux of pollutants, inappropriate model parameters, lack of weather and precipitation coverage, difficulties with interpretation of precipitation quality monitoring data (background and dust contamination).

Table 3. Observed and predicted wet deposition of sulphur at the precipitation quality monitoring stations for 1985 summer (June, July and August).

Monitoring Station	Observed	MESOPUFF (g SO <sub>4</sub> <sup>2-</sup> m <sup>-2</sup> )	RELMAP	ARM3
Hay River	0.11	0.36×10 <sup>-3</sup>	-*	0.0
Ft McMurray	0.35	0.52×10 <sup>-1</sup>	0.42×10 <sup>-1</sup>	0.31×10 <sup>-1</sup>
Edson	0.34	0.72×10 <sup>-4</sup>	0.38×10 <sup>-3</sup>	0.10×10 <sup>-1</sup>
Cree Lake	0.16	0.96×10 <sup>-2</sup>	0.23×10 <sup>-1</sup>	0.32×10 <sup>-2</sup>
Edmonton	0.30	0.26×10 <sup>-2</sup>	0.32×10 <sup>-3</sup>	0.49×10 <sup>-2</sup>
Cold Lake	0.14	0.26×10 <sup>-2</sup>	0.15×10 <sup>-2</sup>	0.37×10 <sup>-2</sup>
Whitecourt	1.33	0.98×10 <sup>-4</sup>	0.74×10 <sup>-3</sup>	0.30×10 <sup>-1</sup>

\*below formatted output limit.

Table 4. Annual observed and predicted wet deposition of sulphur at the precipitation quality monitoring stations.

Monitoring Station	Observed	SERTAD (g SO <sub>4</sub> <sup>2-</sup> m <sup>-2</sup> )	RELMAP	ARM3
Hay River	0.77	0.60×10 <sup>-2</sup>	0.85×10 <sup>-3</sup>	0.86×10 <sup>-4</sup>
Ft McMurray	0.81	0.23	0.11	0.34×10 <sup>-1</sup>
Edson	0.70	0.71×10 <sup>-2</sup>	0.90×10 <sup>-3</sup>	0.16×10 <sup>-1</sup>
Cree Lake	0.25	0.70×10 <sup>-1</sup>	0.43×10 <sup>-1</sup>	0.55×10 <sup>-2</sup>
Edmonton	0.66	0.59×10 <sup>-2</sup>	0.15×10 <sup>-2</sup>	0.12×10 <sup>-1</sup>
Cold Lake	0.39	0.20×10 <sup>-1</sup>	0.90×10 <sup>-2</sup>	0.38×10 <sup>-2</sup>
Whitecourt	2.21	0.87×10 <sup>-2</sup>	0.25×10 <sup>-2</sup>	0.60×10 <sup>-1</sup>

#### 4. DISCUSSION

ARM3 was adapted to northern Alberta and Saskatchewan, and simulations were conducted with available meteorological data from 1985. Emission sources considered were limited to the oil sands extraction plants near Fort McMurray. Monthly, seasonal, and annual concentration and deposition patterns of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  were computed using model default parameters. The seasonal and annual amounts of wet deposition at the precipitation quality monitoring stations predicted by the model differed significantly from observations. The distributions of concentrations and depositions simulated by ARM3 did not agree with those by RELMAP, MESOPUFF-2 or SERTAD either.

ARM3 predicted that a maximum annual mean ground level  $\text{SO}_2$  concentration of  $6.0 \mu\text{g m}^{-3}$  occurred near the Whitecourt area, a considerable distance to the southwest of the emission sources. Near the emission sources  $\text{SO}_2$  concentrations were low, about  $0.3 \mu\text{g m}^{-3}$ . However, both RELMAP and SERTAD indicated that the location of the maximum annual mean  $\text{SO}_2$  concentration was within 100 km from the emission sources. RELMAP predicted that a maximum  $\text{SO}_2$  concentration of  $1.2 \mu\text{g m}^{-3}$  was located to the southeast of the source region near Fort McMurray, while SERTAD predicted value of  $3.0 \mu\text{g m}^{-3}$  was due east. Topographical effects were not included in RELMAP and SERTAD. Thus, the disagreement between the ARM3 simulation results and those of RELMAP and SERTAD may be attributed to the topographically induced air flow. Similar conclusion can be drawn when comparing the annual mean sulphate concentration, and wet and dry depositions of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ .

Because ARM3 was designed to simulate acid deposition and pollutant concentrations in regions within the Rocky mountains, the model was specifically

formulated to run with a rugged topography. An attempt to run ARM3 without any terrain, so that comparison results in this study can easily be interpreted, failed. It appears that the model cannot be applied to a flat area.

ARM3 is a relatively new model and has not undergone any rigorous operational testing, sensitivity analyses, or verification studies. Because of the time constraint in this study, the source code of the model supplied by the U. S. Environmental Protection Agency was directly compiled into the computer system, without any thorough check. Thus, it is possible that coding errors have not been identified and subsequently corrected.

Default model parameters were used in this study. ARM3 was developed to calculate incremental acid deposition (sulphur and nitrogen species) and pollutant concentration impacts in complex terrain of the U. S. Rocky Mountain region. Several parameters in the model have been set to the optimal values for the Rocky Mountains. In additions, the interpolation of temperature, dew point temperature, and precipitation amounts involves orographic adjustments based on climatological data from the Rocky Mountain region. As an example, the algorithm for interpolating precipitation was derived from analysis of a year's worth of 24-hour precipitation data. It produced annual precipitation fields over the Colorado mountains that agree reasonably well with the climatological averages. Nevertheless, it has been recommended that the user should evaluate precipitation field for each new application. Therefore, some of these model parameters and orographical adjustments may not be appropriate for region in this study.

To summarize, major reasons for the disagreement between the ARM3 and RELMAP prediction results probably come from: (1) the inclusion of topographical influences in ARM3; (2) possible coding errors in ARM3; and (3) inappropriate



model default parameters used in the study area.

Substantial computational time and disk storage are required by the ARM3 simulations. It required about 25 MB of disk storage to run a monthly simulation. Note that only two emission sources, 3 upper-air and 20 surface meteorological and precipitation stations were used. The CPU usages for the 1985 monthly simulations are given in Table 5. For the same runs, RELMAP took approximately 10 to 15 minutes on the VAX-11/780 computer, which is about 4 times slower than the VAX 6210 computer used in this study. ARM3 is even more demanding on computer time than the MESOPUFF-2. MESOPUFF-2 required 4 to 7 hours on the VAX-11/780 for the summer month simulations, which would be 1 to 1.8 hours on the VAX 6210.

Table 5. CPU usage for the 1985 simulations of the VAX 6210 computer system.

Month	CPU	Month	CPU
January	2.5	July	2.7
February	2.9	August	1.8
March	3.4	September	2.8
April	3.3	October	2.8
May	3.3	November	1.8
June	2.2	December	2.0

Judging from run times, ARM3 is not very practical for linking emissions to pollutant loadings in Alberta. It will be too costly to run the model for an area of approximately 3,000×2,000 km<sup>2</sup>, and 50 emission sources. Furthermore, use of the model for impact assessments at large downwind distances, where the Gaussian puff assumption may be violated because of the influence of wind shear and loss of parcel integrity, should be avoided. However, the physical and



chemical processes involved in the model are sound. For single sources in the Rocky Mountain region, or the impacts of future economic development in the foothills, ARM3 could be useful. Regardless, further testing of the model would be required.

## 5. CONCLUSIONS AND RECOMMENDATIONS

To summarize, ARM3 has been compared with RELMAP as practical mesoscale deposition model for use in northern Alberta and Saskatchewan.

ARM3 was adapted to northern Alberta and Saskatchewan, and simulations were performed with 1985 meteorological and emission data from the oil sands extraction plants. Comparisons with observations and RELMAP simulation results from an earlier study were made. The predicted seasonal and annual amounts of wet deposition at precipitation quality monitoring stations differed significantly from observations. Possible reasons for the disagreement between the prediction and observation are: model coding errors, inappropriate model default parameters used in the study area, limited emission source, excluding background and laterals boundary flux of pollutants, lack of weather and precipitation coverage, difficulties with interpretation of precipitation quality monitoring data (background and dust contamination). The distributions of concentrations and depositions simulated by ARM3 did not agree with those by RELMAP and other models. Major reasons for the disagreement probably come from: the inclusion of topographical influences, possible coding errors, and inappropriate model parameters used in the study area.

Considerable computational time and disk storage are required by the ARM3 simulations. The model is not suitable for impact assessments at large downwind distances. However, if interests are focussed on single sources in the Rocky Mountain region, or on impacts of future economic development in the foothill areas, the use of ARM3 would be recommended.

Based upon the experience gained in the this study, the following specific

recommendations are presented:

1. If such a use is contemplated, ARM3 can be a valuable tool for the projection of impacts of industrial developments in the Alberta foothills or for small scale applications (small area and limited emission sources). It is recommended that ARM3 be tested for possible coding errors and that appropriate model parameters be developed for Alberta settings.
2. It is recommended that the field monitoring program includes stations at the location of maximum predicted deposition - Whitecourt-Hinton and Fort McMurray. Each station should at least be equipped to measure concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , and estimates of dry deposition of total sulphur, as well as wet deposition.
3. The processing of meteorological data is extremely demanding, both in computational time and storage. It requires more disk space and CPU time for extracting and formatting a month's meteorological data than for the model simulation. Thus, it is recommended that an one-year meteorological period which is representative of the anticipated long-term conditions in Alberta be selected. Future scenario simulations of environmental loadings from projected emissions should be performed on the basis of this climatological representative meteorological data. It should be noted that using an "average" meteorological year

will eliminate the effects of a specific condition associated with a particular episodic events. Should this type of application be required, meteorological data connected with such condition must be used in the simulation.

4. A model prediction is only as good as the input data. It is recommended that emissions, together with released conditions, be collected and updated on the time and space scales used by the model.

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## 7. APPENDICES

### 7.1 ARM3 SEASONAL SIMULATION RESULTS

Simulated seasonal mean  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  concentrations and seasonal dry, wet and total depositions generated by ARM3 are given in this appendix (Figures 8 to 12). Simulations were conducted for the year of 1985.



WINTER



SPRING

Figure 8. Simulated seasonal average SO<sub>2</sub> concentration ( $\mu\text{g m}^{-3}$ ).  $\square$ s denote monitoring stations and +'s are emission sources.

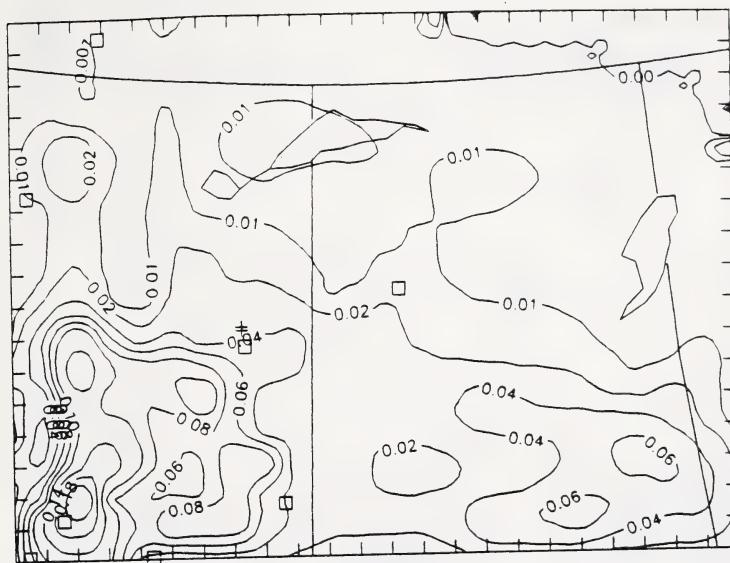


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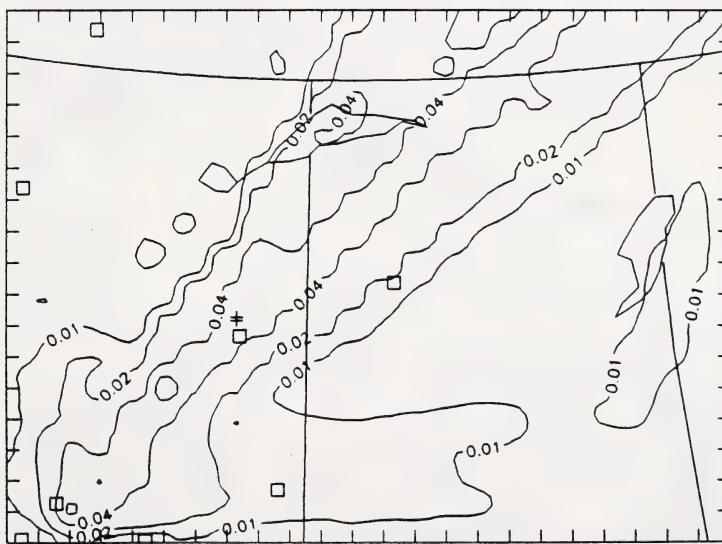


AUTUMN

Figure 8. Continued.



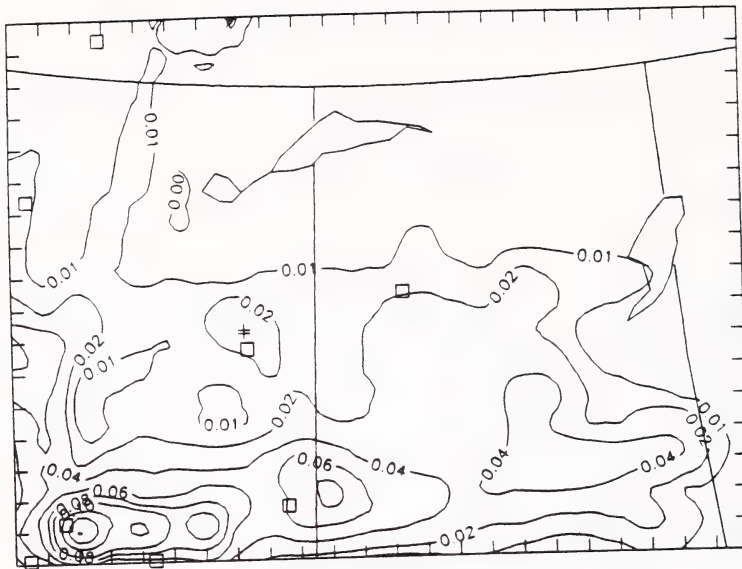
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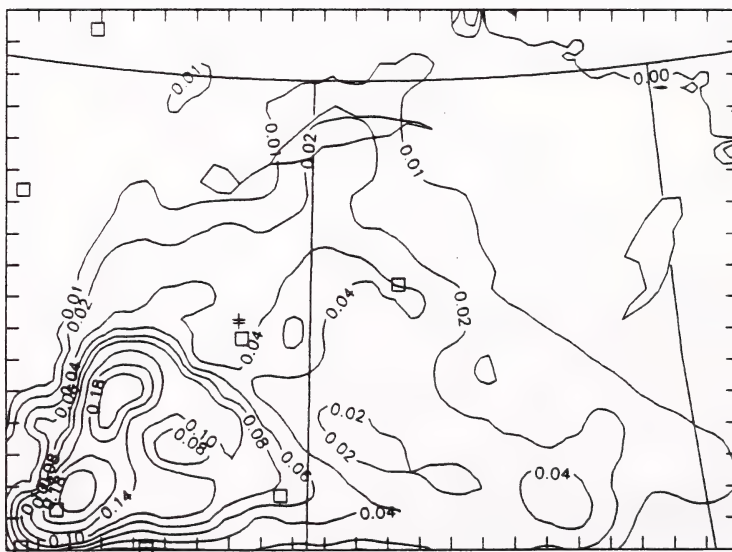
SPRING

Figure 9. Simulated seasonal average  $\text{SO}_4^{2-}$  concentration ( $\mu\text{g m}^{-3}$ ).  $\square$ s denote monitoring stations and +s are emission sources.



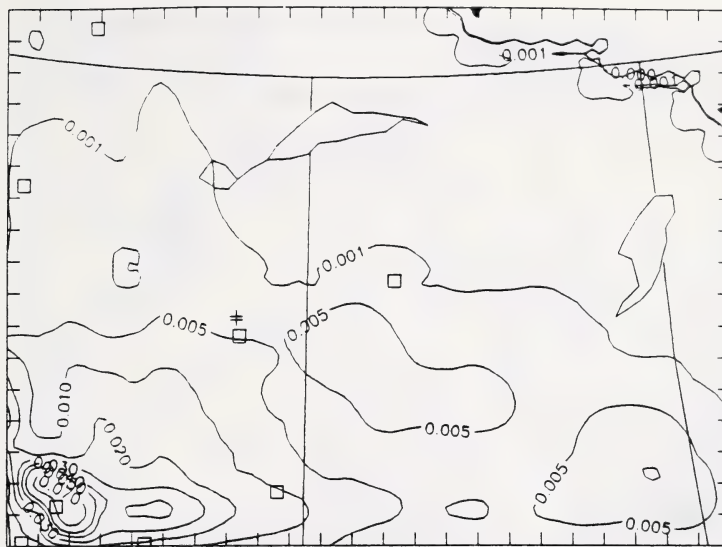


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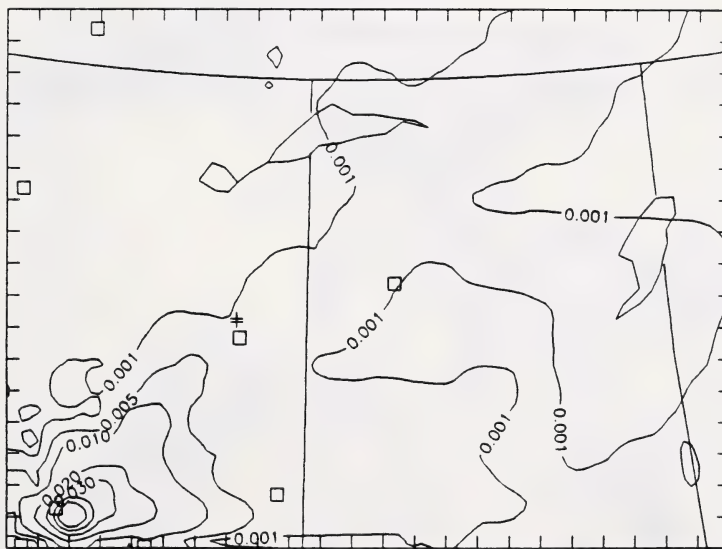


AUTUMN

Figure 9. Continued.

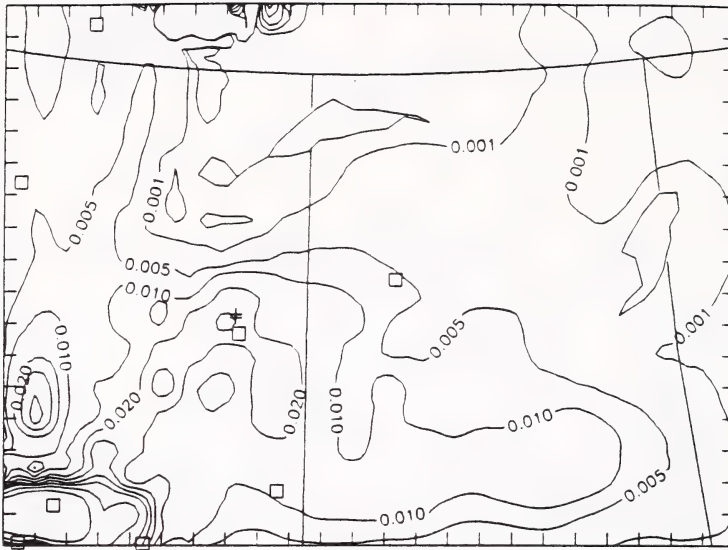


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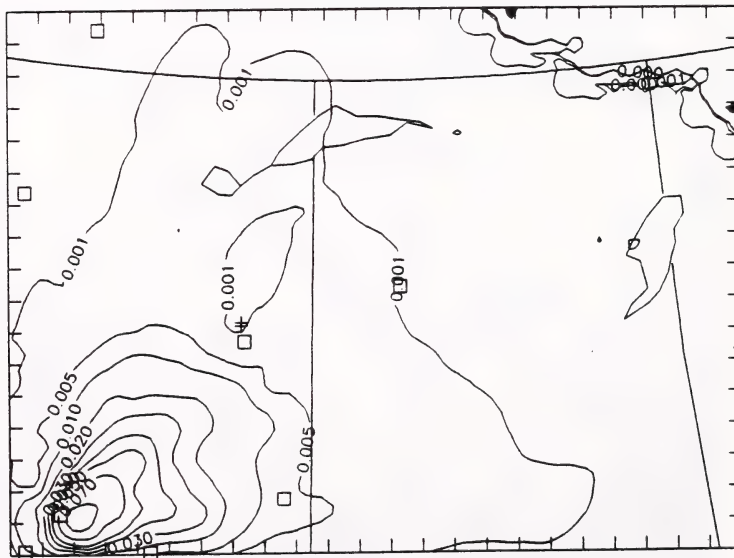


SPRING

Figure 10. Simulated seasonal dry deposition of sulphur ( $\text{kg ha}^{-1}$ ).  $\square$ 's denote monitoring stations and + 's are emission sources.

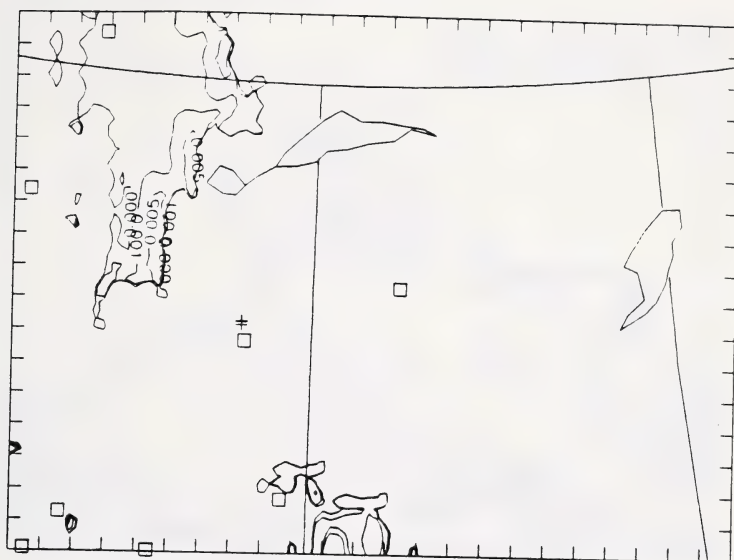


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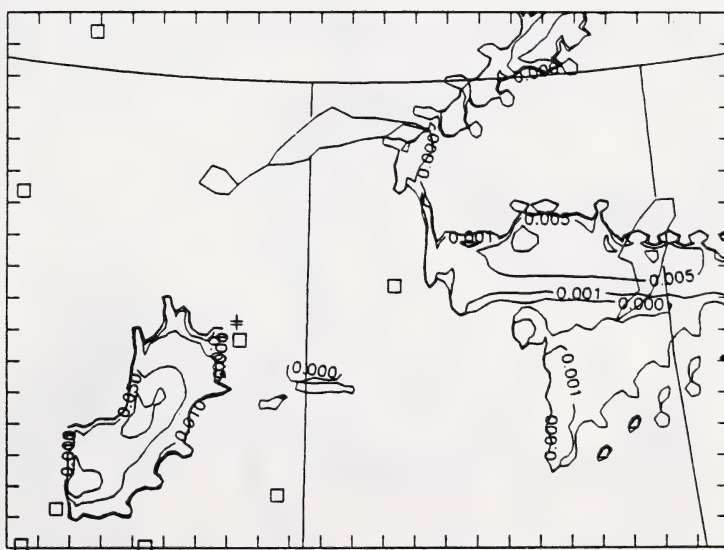


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Figure 10. Continued.

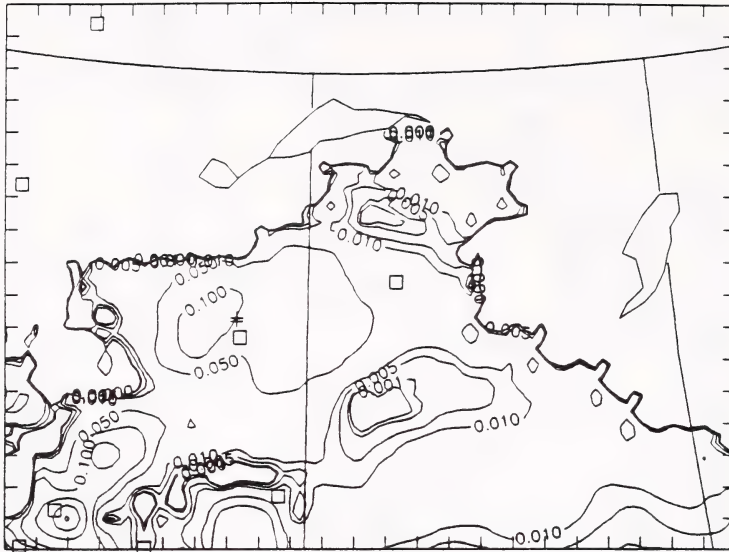


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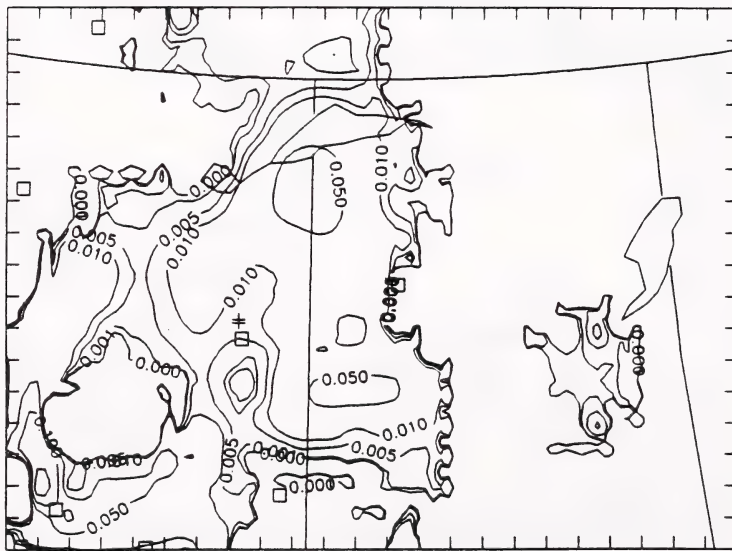


SPRING

Figure 11. Simulated seasonal wet deposition of sulphur ( $\text{kg ha}^{-1}$ ). □'s denote monitoring stations and +'s are emission sources.



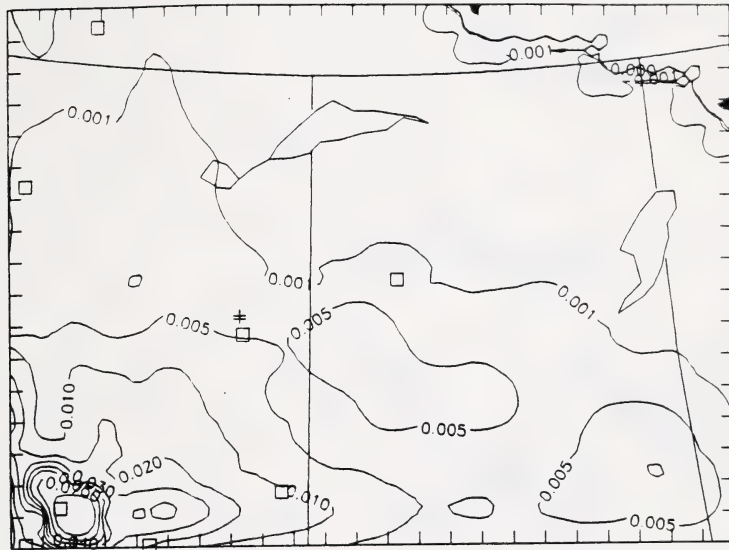
SUMMER



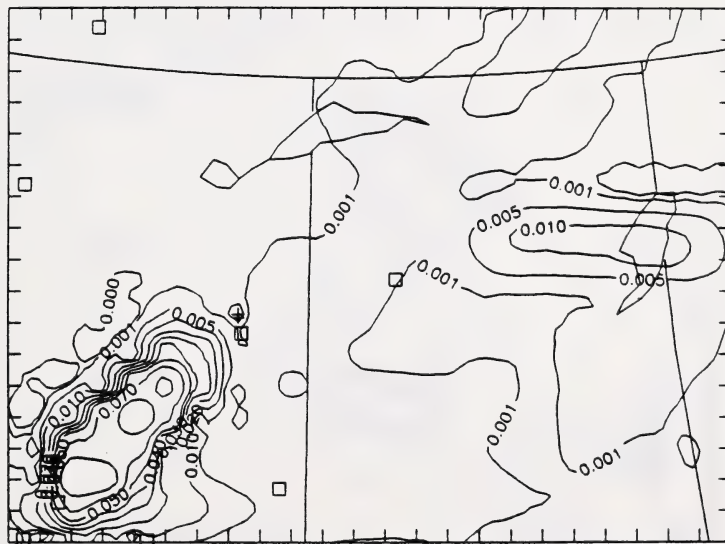
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Figure 11. Continued.



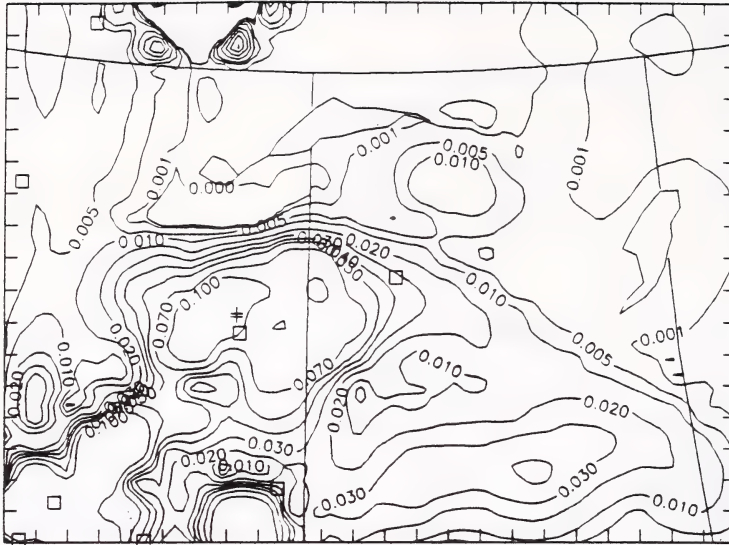


WINTER

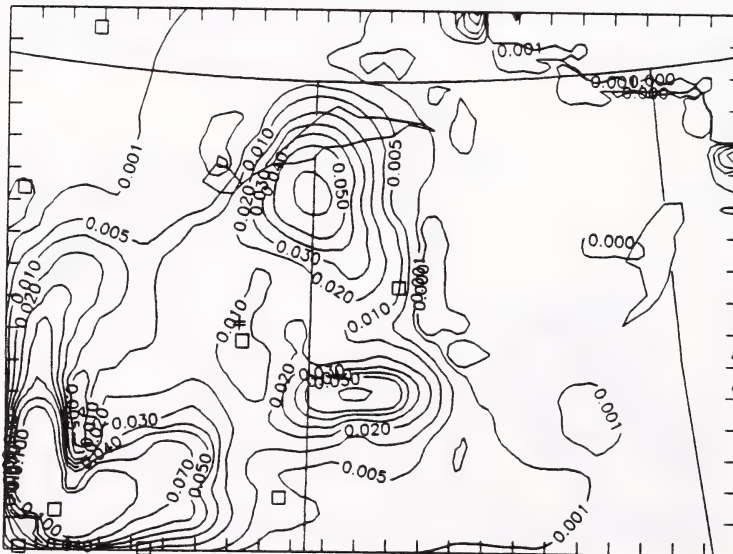


SPRING

Figure 12. Simulated seasonal total deposition of sulphur ( $\text{kg ha}^{-1}$ ). □'s denote monitoring stations and +'s are emission sources.



SUMMER



AUTUMN

Figure 12. Continued.





## **SECTION 3**

**Acid Deposition Impacts on Alberta Soils:  
Long Term Response, Critical Loadings, and Target Loadings**





ACID DEPOSITION IMPACTS ON ALBERTA SOILS:  
LONG TERM RESPONSE, CRITICAL LOADINGS, AND TARGET LOADINGS

by

L.W. TURCHENEK

S.A. ABOUD

Environmental Research and Engineering Department  
Alberta Research Council

and

G. LUTWICK

Soil Protection Branch  
Wastes and Chemical Division  
Alberta Environment

for

Acid Deposition Program Management Committee  
Alberta Environment

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## EXECUTIVE SUMMARY

The objective of the soils component of the Acid Deposition Program is to improve the capability to predict the long term response of soils in Alberta to acid deposition in order to enable improved soil sensitivity, critical loading, and target loading determinations. Sub-objectives of the soils project are:

- (1) To acquire a knowledge and data base of inorganic soil properties and processes in order to enhance performance of a predictive model of acid deposition impacts on soils;
- (2) To acquire a knowledge and data base of organic soil properties and processes in order to enhance performance of a predictive model of acid deposition impacts on soils;
- (3) To validate model performance for Alberta conditions by conducting acidification experiments in a forest soil;
- (4) To assess the ability of soils at Alberta Environment's long term acidification monitoring sites to behave as early warning sites by application of the predictive model;
- (5) To derive critical loads for a range of Alberta soils (in order to serve as criteria for the subsequent derivation of target loadings).

These objectives address the Acid Deposition Program goal to provide scientific and technical knowledge for limiting acid deposition to protect sensitive forest, lake and soil systems in Alberta. Soil process models have been applied previously in Alberta and are considered to be the most effective mechanism for assessing impacts of acid deposition and for determining critical loads for soils. However, deficiencies in the model applied (ARC model) have been identified, namely lack of inclusion of all soil buffering mechanisms, and lack of model input data specifically applicable to soils in Alberta. Other models were reviewed in this project to determine if some of them might be more appropriate for application in Alberta than the currently used model. Requirements for evaluating Alberta soils include ability to analyze changes over time and ability to derive critical loads, the latter being the basis for addressing the issue of establishing target loadings in Alberta.

Although both steady state and dynamic models can be used to determine critical loadings, dynamic models are needed to estimate changes over time. In evaluating dynamic models, use of readily available data is important in Alberta since there is a need to evaluate many types of



soils occurring over a broad area, and the effort to obtain large amounts of data would require much time and resources. The use of the previously applied model, the ARC model, is considered to be appropriate for further use as it has been previously applied in Alberta. However, it is necessary to evaluate nutrient cycling in soils which is not currently included in this model. It is suggested that one or more other models that account for nutrient cycling be acquired to enable evaluation of this process and comparison of results with the ARC model. Two models in particular are recommended, namely the RESAM model developed in The Netherlands and the ILWAS model developed in the USA.

Investigations of inorganic soil properties aimed at improving performance of a soil acidification simulation model were initiated by the study of sulphate sorption in soils. The soils consisted of Brunisolic, Podzolic and Chernozemic soils, five of which were sampled during 1991 and the other eight obtained from archived samples of the Long Term Soil Acidification Monitoring Program of Alberta Environment. It was found that sorption is negligible in the Alberta soils studied. This effect is a consequence of these soils not containing the required minerals for adsorption, or to a possibility that they have already been fully sorbed with sulphates. The assumption of negligible soil adsorption of sulphates used in the ARC model is thus valid. The implications of this data are that acid inputs (in sulphate form) are not buffered by adsorption in our soils and thereby could contribute to cation leaching.

Organic soil materials consist of two main types; forest floor materials and peat soils. A conceptual model of acidification in organic soil materials has the following elements: bicarbonate buffering; ion exchange and metal complexation; assimilatory uptake of ions by vegetation; redox processes, and; organic acid buffering. The conceptual outline of major buffering processes presented provides a mechanism for focussing research on relevant processes and on the relationships among processes.

Field experimentation aimed at validating the soil acidification model used in Alberta was initiated in 1991. Plot establishment, acid application and soil sampling were carried out. Application of the ARC soil acidification model to the plot soil indicated that all of the four year period of the Acid Deposition Project will be required to obtain measurable differences in soil properties for model validation. Collection of meteorological data at the plot site is recommended, and it is hoped that air quality and precipitation chemistry data will be collected in the same region as the field plot site. Availability of such data would enable more precise values to be used in testing the model.

To address the fourth objective above, the ARC model was applied to soils of the Alberta Environment Long Term Monitoring Program. These soils span a range of buffering capabilities as based on exchangeable base cation saturation levels. Most of the soils in the program appear to be appropriate as early warning indicators. An exception is the Twin Butte soil which is strongly buffered and would not likely show chemical changes even under very high acidic loadings. In measuring changes over time, pH in most soils will not show large decreases if they are in fact influenced by acidic inputs. The base saturation levels on the other hand may provide a more sensitive measure of changes due to acid inputs.

The results of simulations using the ARC model were in agreement with results of previous studies in which coarse-textured soils within various soil orders were found to be the most readily affected by acidic inputs. It is predicted that changes due to acid stress will be greatest in sandy soils of the Dystric Brunisol and the Orthic Humo-Ferric Podzol taxonomic groups. Significant reductions in pH and base saturation occurred in these soils within 100 years in the simulations. The model results show that some of these soils may be acidified even at the current acid loading rates. Increases in soluble  $\text{Al}^{3+}$  to potentially toxic concentrations in these soils were also indicated by the simulations. These results suggest that the critical load for some soils could be as low as  $0.2 \text{ kmol ha}^{-1} \text{ yr}^{-1}$ , which is less than a previously determined loading of  $0.3 \text{ kmol ha}^{-1} \text{ yr}^{-1}$ .

The two Chernozemic soils examined in this study were well buffered. The coarse-textured Esther soil had a relatively high cation exchange capacity and exchangeable base cation level as a consequence of relatively high organic matter content in the surface horizon.

More information about soluble Al levels in low pH soils is needed in order to evaluate the critical loading rates based on Al. The model shows that some very low pH soils could have Al approaching levels toxic to plants. Further elucidation of the relationship of soluble Al to pH in Alberta soils is required in order to establish realistic model results.



## 1. INTRODUCTION

### 1.1 OBJECTIVES

The objective of the soils component of the Acid Deposition Program is to improve the capability to predict the long term response of soils in Alberta to acid deposition in order to enable improved soil sensitivity, critical loading, and target loading determinations.

The sub-objectives are:

- (1) To acquire a knowledge and data base of inorganic soil properties and processes in order to enhance performance of a predictive model of acid deposition impacts on soils;
- (2) To acquire a knowledge and data base of organic soil properties and processes in order to enhance performance of a predictive model of acid deposition impacts on soils;
- (3) To validate model performance for Alberta conditions by conducting acidification experiments in a forest soil;
- (4) To assess the ability of soils at Alberta Environment's long term acidification monitoring sites to behave as early warning sites by application of the predictive model;
- (5) To derive critical loads for a range of Alberta soils (in order to serve as criteria for the subsequent derivation of target loadings).

These objectives address the Acid Deposition Program goal to 'Provide scientific and technical knowledge for limiting acid deposition to protect sensitive forest, lake and soil systems in Alberta'. It more specifically addresses the recommendations of previous research programs, these being summarized in the Alberta Environment Departmental Committee on Acid Deposition (1988), Master List of Recommendations in 'Action Plan for Implementing Alberta's Acid Deposition Management Strategy' and in 'Review and Assessment of Acid Deposition Management Strategy for Alberta' by the Alberta Environment Task Group on Acid Deposition (1988).

This project also links to other Acid Deposition Program goals in that it will both feed and derive information in relation to other program projects. In particular, it is considered necessary to select a location for field experimentation in conjunction with siting of one of the stations in the provincial network for monitoring atmospheric chemistry. Eventual modelling of soil responses to acid deposition will utilize information from the entire network as well as from other sources. The project will also link with any efforts in vegetation and aquatic impact studies in this program.



## 1.2 PROBLEM AND NEED FOR SOILS RESEARCH

The development of target loadings to protect highly and moderately sensitive aquatic and soil systems has been identified as a component of Alberta's acid deposition management strategy as originally recommended by the Western and Northern Canada Long Range Transport of Atmospheric Pollutants (LRTAP) Technical Committee (1990). The nature and extent of acid deposition in Alberta, and the potential impacts on ecosystems, have been previously documented (e.g., Legge and Krupa 1990). The target loading concept as applied to soils has been previously reviewed by Turchenek and Abboud (1988) and Singleton et al. (1988). The establishment of target loadings for soils can be considered as consisting of five main components: 1) development of a reliable method for predicting soil responses; 2) validation of the method for predicting soil responses; 3) quantification of soil sensitivities by examining a range of acid loadings and soil types; 4) derivation of a target loading based on the most sensitive soils as determined in 3) above, and; 5) identification of the most sensitive soils in a particular region by spatial analysis of soils and their target loadings.

Preliminary quantification of soil responses and critical acid deposition loadings has been carried out for some northern Alberta soils using a computer simulation model by Turchenek and Abboud (1988). Subsequent analysis of the results of the above study by Singleton et al. (1988) suggested that the levels of acid deposition to sensitive soils in Alberta should not exceed  $0.30 \text{ kmol (H}^+) \text{ ha}^{-1}\text{yr}^{-1}$ . Thus, some issues related to the determination of target loadings (i.e., methodology, determining sensitivities, and deriving a target loading) have already been addressed. Validation of the model used in the above work has not yet been achieved. The fifth component above has also been addressed on a province wide level (i.e., at a low level of detail) through mapping of different sensitivity categories of soils (Holowaychuk and Fessenden 1987). The efforts to date represent a first approximation of the effects of acid deposition on soils. The modelling procedure used to determine soil responses has some deficiencies in that all buffering mechanisms in soils are not accounted for and coefficients used were not derived for Alberta soils. Refinement of the previously used model or acquisition of a different model is required to achieve the goals of reliable prediction of soil responses to acid deposition and of establishing target loadings. Preliminary work on elucidating different buffering mechanisms and deriving coefficients using Alberta soils has been carried out by Abboud and Turchenek (1988).

This project addresses the first three components of establishing a target loading as indicated above. The largest part of this work involves refinement and verification of a soil response model. This model can be applied in derivation of critical loadings upon which target loadings can be



based. The fourth component, namely the establishment of target loadings, must be based not only on critical loads but also on socioeconomic criteria and, as such, would likely be established by government and industry, with input from soils investigators as well as other terrestrial effects researchers. The fifth component, that is, the derivation of regional target loadings through spatial analysis of soils and their individual target loadings, is not addressed in this project as it must be accomplished through a somewhat different approach and methodology involving geographic information system technology.

Understanding of the responses of organic soil materials to acid deposition in relation to sensitivity and critical loadings is limited. The role of organic materials in the litter (LFH) layers of mineral soils has not been assessed in relation to the predictive model previously applied in Alberta. An initial evaluation of the properties and processes of forest litter materials is addressed in this proposal.

Information on the effects of acid deposition on peat soils is likewise limited. Peatlands account for about 20 percent of the area of the province of Alberta. Considerable attention has been directed to recognizing and assessing the effects of acidic deposition on terrestrial and aquatic ecosystems, but little research has been carried out with regard to the sensitivity of peatlands, which are transitional to these two systems. A preliminary attempt was made to evaluate the sensitivity of peatlands to acid deposition by Holowaychuk and Fessenden (1987). The need for additional information on peatlands with regard to distribution, extent, types, chemistry, nutrient cycling, organic cycling and water balance has also been indicated in reports by Holowaychuk and Fessenden (1987) and Turchenek et al. (1987). Information on the distribution, extent and types is available in a map recently produced for Alberta Environment by Turchenek and Pigot (1988) and in the report of Turchenek (1990).

Little research has been carried out to determine the buffering capabilities and to quantify responses of organic soils to acidic inputs. This proposal addresses this need in terms of 1) developing a conceptual model of responses of peat soils, as well as LFH materials, to acid deposition; 2) measuring buffering capacities and related properties in some of the main types of organic materials; and 3) using these data to evaluate target loadings as well as the provisional sensitivity rating system of Holowaychuk and Fessenden (1987).

Long-term soil acidification monitoring is being conducted by the Soil Protection Branch, Wastes and Chemicals Division, Alberta Environment. Sites have been established at eight locations around the province, and a report on the first eight years of monitoring has been prepared by

Roberts et al. (1989). Site selection criteria included the inferred sensitivity of soils to acid deposition. These soils have not been quantitatively assessed in terms of specific buffering mechanisms and in terms of how soon changes in soil properties might occur as a result of atmospheric inputs of acidity. It was recommended by Roberts et al. (1989) that further analysis and investigations (e.g., sulphate adsorption isotherms, buffer curves, simulation modelling) be undertaken to assess the suitability of each monitoring site as to its ability to act as an early warning to the potential adverse effects of acidic deposition. The suitability of the above sites as early warning indicators is assessed in this project by application of the predictive model referred to previously. Furthermore, the specific mechanisms of buffering in these soils are ascertained by inclusion of soils from the long term sites in the work on model refinement and target loading determinations referred to above.

### 1.3 GENERAL APPROACH

The soils project was developed with an expected duration of four years. The project is divided into five activities dependent on the nature of the soil material and/or the activities involved. These activities are: 1) Inorganic research; 2) Organic research; 3) Model validation; 4) Monitoring site evaluation, and; 5) Critical load determinations. These five components are described below.

#### 1) Inorganic Research

Inorganic research refers to activities aimed at improving the reliability of the applied model for predicting soil responses to acid inputs. The determination of the roles of inorganic soil components constitutes this component. The main activity involves acquisition of data required for model equations through laboratory analysis and experimentation on buffering mechanisms and relationships among variables in Alberta soils.

#### 2) Organic Research

This component consists mainly of a laboratory based approach whereby some basic information about organic soil systems and their interactions with acid forming substances can be attained within 3-4 years. This information will enable prediction of critical loading values based on simulating the significant reactions involved in the response of organic soils to acid deposition. The buffering of the liquid and organic phases in organic soils will be assessed, as well as the nature and magnitude of the organic acids present and their complexation capacities.

3) Model Validation

Confidence in the results provided by predictive models is required for applications such as the derivation of critical loads. Validation of a model is usually carried out by using it to make a prediction about the real-world system and checking the result by direct experimentation or by reference to already-collected data. The model validation is carried out by experimentation with forest soils as these have been identified as being potentially the most sensitive to acid deposition. The experimental approach entails artificial acidification of field plots using a range of acid input levels, monitoring the effects on soil properties, comparing the results with model predictions, and adjusting the model if necessary. Applying this approach to soils of interest within Alberta is preferred to other possibilities such as use of results from long-term fertilization in agricultural field trials or use of data from other countries or provinces.

4) Monitoring Site Evaluation

The suitability of the long term soil acidification monitoring sites as early warning indicators will be initially assessed by application of the existing predictive model, and will be reassessed with the updated model upon model refinement and validation. Information on buffering capacities and mechanisms in these soils will be obtained through inclusion of samples from the long term sites in the work described for component 1) above.

5) Critical Load Determination

Upon model validation, predictions of soil responses to acidification in various areas of interest around the province can be carried out. The model will be applied to selected soils described in soil survey reports, and critical loads will be determined by examination of changes in soil properties in relation to known threshold levels for pH, Al toxicity and other parameters.



## 2. INORGANIC SOIL COMPONENT

### 2.1 INTRODUCTION

Research on the inorganic soil component refers to activities aimed at improving the reliability of the applied model for predicting soil responses to acid inputs. The determination of the roles of various inorganic soil components constitutes this component. The main activity involves acquisition of data required for model equations through laboratory analysis, experimentation on buffering mechanisms and determining the relationships among variables in Alberta soils.

Various process-oriented models have been developed to predict the long-term effects of acid deposition on soils. Soil process models that have been developed to describe acid deposition responses deal mainly with soil chemistry, while representation of other soil attributes such as organic matter decomposition, microbial dynamics or solute transport has been either limited or not attempted. Some models have been built to describe soil processes only while others have been developed as part of comprehensive watershed impact models. Various models were reviewed by Turchenek et al. (1987) as part of the Alberta Government/Industry Acid Deposition Research Program. Since that time numerous other models have been developed, particularly in Europe, and have been reviewed in a number of publications. Both the earlier and more recently developed models are reviewed in the following sections.

### 2.2 REVIEW OF MODELS

#### 2.2.1 Types of Models

Steady state and dynamic methods are two main approaches to modelling of soil processes. Steady state models are those in which all time-variant processes are ignored and only long term average fluxes are considered. Dynamic methods have time-variant processes included (Sverdrup et al. 1990; de Vries and Kros 1991).

Sverdrup et al. (1990) referred to the steady state method more specifically as the 'steady state mass balance method' since it uses the static mass balance between long term inputs of acidity and long term in-soil production of alkalinity. It applies to soils, groundwater, lakes and surface water runoff from catchments. The dynamic modelling method applies to all kinds of systems and is the only way to address the problem of episodic events. The approach requires more input data and time for application than the other methods.

Steady state methods consider only the final result of a certain deposition level and do not consider the time frame within which that result is reached. The methods are based on the chemical and geochemical properties of soils and an understanding of the major processes involved in production and consumption of acidity in the soils. Mineral weathering is considered to be the major long term source of alkalinity that neutralizes acidity in the soil system, as well as the major source of base cations to replace those removed by leaching.

The dynamic modelling method considers time-variant processes, and is the best way of addressing the significance of episodic events under different deposition scenarios. All basic methods can be used to assess the effect of different abatement strategies (Sverdrup and Warfvinge 1988; de Vries 1988); however, dynamic models are required for the assessment of temporal aspects of abatement strategies and different deposition scenarios.

#### 2.2.2 Steady State Methods

The basic principle of the steady state method involves identifying the long term average sources of acidity and alkalinity in the soil system. Several assumptions have been made in the steady state calculations: 1) ion exchange is at steady state and there is no net change in base saturation or no net transfer of acid neutralizing capacity from soil solution to the ion exchange complex; 2) there is no net denitrification, and adsorption or desorption of nitrogen; i.e., the nitrogen cycle is at steady state; 3) sulphate is also at steady state, there being no significant sulphide oxidation, sulphate uptake, sulphate fixation or sulphate reduction; 4) a simple hydrology is assumed and there is only direct infiltration of moisture through the soil profile, and; 5) there is soil solution equilibrium at all times (Sverdrup and Warfvinge 1988; Sverdrup et al. 1990).

The steady state model is used to calculate soil acidification which is defined as an increase in total adsorbed acidity in the soil in relation to the content of adsorbed base cations in ion exchange positions, generally interpreted as a decrease in base saturation. In an acidification process, a soil may initially acidify as it adsorbs hydrogen ions in exchange for base cations. Thus leachate in the soil that is undergoing acidification may stay semi-neutral due to the in-situ neutralization of the percolating solution. Later, as the base cation supply becomes exhausted the acid percolate will no longer be neutralized. If the total net inputs of acid to the soil are balanced by the long term total net inputs of alkalinity production in the soil system, no change in adsorbed acidity or base cations will take place (Sverdrup et al. 1990).



Sverdrup et al. (1990) described three steady state models developed in Europe.

- 1) SMB model.
- 2) MACAL model.
- 3) PROFILE model.

In North America, McFee et al. (1977) described a simple approach while Arp (1982) and Reuss and Johnson (1986) documented more complex models based on processes on the ion exchange complex and in soil solutions. The geochemical model of Sposito and Martignod (1979) can be used for acid deposition evaluations of soil impacts. These are labelled:

- 4) McFEE model
- 5) ARP model
- 6) REUSS AND JOHNSON model
- 7) GEOCHEM

SMB stands for the Simple Mass Balance model, and it involves balancing acidity versus alkalinity, as in a titration. It is calculated manually and can be used for quick evaluation of scenarios involving relatively higher and lower levels of acidity and neutralizing capacity to arrive at critical loads. This is a one-layer model wherein only a specified thickness of the soil profile can be considered. This approach has mainly been used in The Netherlands and Sweden for calculating critical loads.

In the McFee model, reduction in soil base saturation is calculated from given inputs of acidity which are assumed to completely replace bases on the exchange complex. Change in pH is approximated from a curve of soil pH versus base saturation determined for soils in the area of study. The approach is simple, makes many assumptions, and ignores weathering and other acid neutralizing reactions, but provides a quick assessment of specific soils and enables comparisons to be made among them.

The ARP model predicts acid cation loss, base cation loss, and change in base status from acid input rates using an approach that qualitatively follows a Freundlich-type adsorption isotherm. Base cation addition by weathering is included in the model, while nutrient cycling is accounted for by considering that in the steady state, organic matter inputs to the soil will equal CO<sub>2</sub> losses from the soil. The time for one base saturation state to change to another can be calculated from the model, and an extended version of the model could allow acid and base inputs to be time dependent thus providing dynamic modelling capabilities.

The REUSS and JOHNSON model calculates changes in base saturation from ionic levels in soil solutions which change with acidic additions to the soil. The model is basically a type of chemical speciation procedure and does not include codes for time dependence of chemical species additions and processes. Weathering and nutrient cycling can be accommodated by separate assessments and by considering their contributions in terms of the specific species included in the model.

GEOCHEM is the most common of several geochemical models that is applied to soils. It is used to calculate chemical equilibria, reactions, and chemical species in solutions, and has been used to predict the speciation of soil solutions affected by acid deposition (Sposito et al. 1980). Separately determined weathering, nutrient cycling and atmospheric additions of chemical species can be input in the model and new equilibria are calculated.

MACAL and PROFILE are multi-layer models. The MACAL model is used mainly in Sweden and the PROFILE model in The Netherlands (Sverdrup and Warfvinge 1988; De Vries 1988).

In these models a mass balance is made on a layer by layer (or horizon) basis for different soil processes. The weathering rate is an input parameter to MACAL, whereas PROFILE generates this from mineralogy and texture. Steady state base saturation is calculated using ion exchange equilibria according to Gaines-Thomas and Gapon equations. The internal cycling of nutrients in the system are included in MACAL, and PROFILE considers nitrification of ammonium and nitrogen uptake. This means that acidity input from base cation uptake is divided into total base cation uptake and litterfall base cation return, and that the net acidity from N transformations is split into ammonium and nitrate uptake and return by litterfall.

### 2.2.3 Dynamic Modelling Methods

Dynamic models are used to calculate the complete acidification process path for an ecosystem through time. The dynamic models, as compared to steady state models, require more input data of which several parameters are more difficult to obtain. However, they are the best tools available for addressing time-dependent scenarios and the impact of episodic events on ecosystems. An assessment of the time periods involved in recovery and response can be made with these models. Several of the models listed here are research tools, and are not operationally available at the present time for outside users.

In the dynamic modelling method, the gradual change with time in the acidification state of the system in response to some change in deposition is calculated with mathematical models. Critical loads can be calculated from scenarios corresponding to different deposition, and the calculated results can be compared to the critical limits at several different points in the system simultaneously. Dynamic models generally incorporate modules to calculate changes in ion exchange, weathering of soil minerals, uptake and cycling of base cations and nitrogen by plants, and soil solution equilibrium chemistry. They use integrated mass balances for substances and differential equations for the rates of different processes. The time-dependent scenarios are obtained by numerical integration of the equation groups advancing in small time-steps through the use of computers.

Various assumptions are made in dynamic models. It is generally assumed that the CEC is constant over time and that a certain ion exchange equilibrium applies (Gapon or Gaines-Thomas). Aluminum is assumed to be in continuous equilibrium with a mineral of the same composition as gibbsite in most models. Some models assume sulphate adsorption to be negligible or at steady state, while others have sulphate adsorption as the major process.

Some soil models are sub-routines of more complex models used for impact studies and critical load determinations for aquatic systems. Sverdrup et al. (1990) suggest that several models be examined before choosing a model for soil evaluations and critical load calculations. The available models differ somewhat in their basic principles, and have different types of limitations connected to their use and to the interpretation of their output results. Such factors must be carefully studied before a model is chosen for a specific type of system.

The operationally available models developed in Europe for scenario assessments are as follows:

- 1) RAINS/SMART
- 2) MAGIC
- 3) SAFE
- 4) MIDAS
- 5) RESAM

Other models developed in the USA include:

- 6) ILWAS
- 7) BLOOM-GRIGAL
- 8) LEVINE AND CIOLKOSZ



The model of Bloom and Grigal (1985) and substantially modified for use in Alberta by Turchenek and Abboud (1988) and Abboud and Turchenek (1990) is referred to as the:

9) ARC model

The above models fall in two distinct groups, namely the simpler models such as MIDAS (Holmberg et al., 1989), SMART (de Vries et Kros 1989) and MAGIC (Cosby et al. 1985), and the more complex models such as RESAM, ILWAS and SAFE.

The MAGIC model is generally used as a one-box model (Cosby et al. 1985; Hornberger et al. 1986), and works with average soil profile chemistry, as the compartment is assumed to be continuously mixed, homogeneous, and of constant density. The model ignores the nitrogen cycle.

MIDAS is also a one-box model, based on acidity as the main variable, and similar in structure to SMART and MAGIC (Holmberg et al. 1989). The model uses either the Gaines-Thomas equilibrium ion exchange approach or an optional kinetic approach. The weathering rate is set at a constant level. The model ignores the nitrogen cycle.

SMART, which is inside the RAINS framework (RAINS is a comprehensive model for examining various ecosystem and emission scenarios in Europe), is also a one-box model, and has many similarities to the MAGIC model (de Vries and Kros 1989). MAGIC and SMART have been applied extensively in Europe to examine soil influences in catchments and lakes. They are among the least input-data-intensive of the dynamic models, due to various simplifications such as nitrogen fixation, adsorption and reduction of nitrogen being negligible, and the water flux being stationary on a yearly basis. SMART also assumes the sulphur adsorption to be at steady state. The ion exchange in MAGIC and SMART is based on the Gaines-Thomas equations.

RESAM is a comprehensive model, incorporating many processes such as nitrogen and base cation cycling between the soil and the canopy, biomass mineralization, and cation exchange equilibrium and flux mass balances for the soil profile. The cation exchange in the model is based on the Gaines-Thomas equations. The master variables of the model are aluminum, base cations and nitrogen. The weathering rate is modelled using a total soil base cation content correlation (de Vries and Kros 1989).

SAFE (Sverdrup et al. 1987) is different from the other models in several principles. The model uses PROFILE as a subroutine for weathering rates and initial conditions. The model uses a kinetic sub-model for the ion exchange of base cations and it converges upon an equilibrium described with the Gapon equation.

RESAM, SAFE and ILWAS have aluminum dynamics controlled either by gibbsite or by a kinetic equation. In SAFE this is a combination of aluminum supply from weathering of primary minerals and aluminosilicates, ion exchange, and precipitation of secondary solids. The choice of the aluminum model (kinetic or gibbsite) is optional. Nitrification and nitrogen uptake is included in the model. RESAM and SAFE both require an external model to generate time-series for the hydrology (precipitation, percolation in each layer, runoff). SAFE uses the PULSE model (a complex hydrology model) for generating input values for soil moisture.

The ILWAS model has a multi-compartment soil module including: ion exchange equilibrium based on the Gaines-Thomas equation; equilibrium or kinetic aluminum dynamics; a canopy module including uptake of base cation and nitrogen; leaf exudation; litterfall and biomass degradation; a snowmelt routine; a 12-layer lake model, and; a kinetic module for nitrification and denitrification. The weathering rate is input to the model, but varied with soil pH (Gherini et al. 1985). Nitrogen deposition and the nitrogen cycle are modelled in SMART, RESAM, SAFE and ILWAS, but not in any of the other listed models. The principles applied are similar to those outlined in the steady state mass balance method section.

The BLOOM-GRIGAL model is a semi-empirical model for predicting changes in soil pH, base saturation, and solution Al levels resulting from acidic precipitation. The changes can be calculated over specified periods of time. The model can accept weathering inputs, but nutrient cycling is not considered except in the sense that it may be assumed to be in a steady state and therefore does not influence soil properties affected by acidification. A major strength of the model lies in its use of readily available data, thus enabling its application on regional scales (Bloom and Grigal 1985).

The LEVINE and CIOLKOSZ model is similar to the BLOOM and GRIGAL model but incorporates additional subroutines to account for more of the processes influencing acidity, namely sulphate adsorption and formation and dissolution of sesquioxides in the soil profile. The model considers two layers whereby acidic deposition reactions are first calculated for the A horizon and the calculated soil solution composition is used as input for the B horizon (Levine and Ciolcosz 1988). As with the BLOOM-GRIGAL model, easily acquired information from soil survey and other sources is used in the model.

The ARC model is derived from Bloom and Grigal (1985) and incorporates empirical relationships for cation exchange and pH based on Alberta soil properties. The model has been



described by Abboud and Turchenek (1990) and Turchenek and Abboud (1988), and is described in part in Section 6 of this report.

Other models such as PULSE (Bergtrom and Lindstrom 1987), BIRKENES (Christophersen et al. 1982) and Enhanced Trickle Down (ETD) were developed for evaluations of aquatic impacts and are not as well connected as the previously discussed models to changes in soil properties. These models, along with ILWAS, depend strongly on calibration to known systems for evaluations of other systems (Sverdrup et al. 1990).

Most of the models require the weathering rate for the whole soil profile as an input parameter. Exceptions are SMART and RESAM in which weathering rate is correlated with and derived from numerous other properties, and SAFE which requires soil mineralogy and texture instead. Accordingly, these are the only models that can predict the initial chemical steady state from soil properties alone.

Most of these models do not include nutrient cycling by the vegetation. The ILWAS model (Gherini et al. 1985) does include nutrient cycling, but this model is not very appropriate for a large scale application because of its extensive data input requirements. The Regional Soil Acidification Model (RESAM) was developed at the Netherlands Soil Survey Institute for analyzing long-term soil responses to acid deposition on a regional scale through use of relatively easily obtained soil data. RESAM is used to predict the annual average fluxes and concentrations of the major elements in soils of characteristic forest ecosystems in the Netherlands. Eventually, the model will be linked as a sub-model in an overall framework predicting impacts from S and N emissions to evaluate the effectiveness of abatement strategies.

#### 2.2.4 Conclusions and Recommendations

A soil process model has been applied previously in Alberta, and modelling is considered to be the most effective mechanism for assessing impacts of acid deposition and for determining critical loads for soils. However, deficiencies in the model applied (ARC model) have been identified, these being related to lack of inclusion of nutrient cycling and organic matter buffering mechanisms, and to lack of data for weathering and ion exchange applicable to soils in Alberta (Turchenek and Abboud 1988; Abboud and Turchenek 1990). Other models were reviewed in this project to determine if some of them might be more appropriate for application in Alberta than the currently used model. Requirements for evaluating Alberta soils include ability to analyze changes

over time and ability to derive critical loads, the latter being the basis for addressing the issues of establishing target loadings in Alberta.

Although both steady state and dynamic models can be used to determine critical loadings, dynamic models are needed to estimate changes over time. In evaluating dynamic models, use of readily available data is important in Alberta since there is a need to evaluate many types of soils occurring over a broad area, and the effort to obtain large amounts of data would require much time and resources. The MAGIC, SMART, BLOOM-GRIGAL, LEVINE and CIOLCOSZ and ARC models are the least input-intensive of the dynamic models. The ARC model is considered to be appropriate for further use as it has been previously applied in Alberta. However, it is necessary to evaluate soil processes not currently included in this model. It would also be helpful if one or both of the more complex models be acquired to enable comparison of results with the ARC model. These two models are ILWAS and RESAM. RESAM was developed as a simpler alternative to ILWAS, requiring input of less complex data and not being dependent on calibration to start the model (Sverdrup et al. 1990). It is not known at this time if RESAM (developed in the Netherlands) is available to users outside of the European network of researchers investigating acid rain. ILWAS, on the other hand, is to be released as a commercial PC-based product during 1992 and will therefore be the most readily available.

In summary, it is recommended that the ARC model continue to be used for general assessments of soil behaviour and critical loads, that modifications based on the properties of Alberta soils be continued, and that the applicability of one or both of RESAM and ILWAS as a comparative tool be investigated during 1992/1993.

## 2.3 EVALUATION OF SULPHATE SORPTION PROCESSES IN SELECTED SOILS OF ALBERTA

### 2.3.1 Introduction

Sulphate and nitrate are generally the dominant anions in acid deposition and are hence of major interest in terms of effects of acid rain on forest-soil acidification, cation leaching from soils, as well as acidity of stream water. Various reports have indicated that the effects of acid deposition on soil cation leaching are strongly mediated by the capacity of the soils to adsorb sulphate in acid soils. In non sulphate adsorbing soils, the introduction of acid sulphate is very likely to result in accelerated cation leaching and increased accumulation of  $H^+$  and  $Al^{3+}$  in the system, whereas in sulphate-adsorbing soils these effects are reported to be less markedly manifested. Input-output

budgets for sulphate in various forest ecosystems have indicated that some ecosystems accumulate sulphur, whereas other ecosystems either show a net loss or maintain a balance in the sulphur budget (Nommik et al. 1988).

A mechanism most commonly responsible for sulphur accumulation in ecosystems is sulphate adsorption in subsoil horizons. Amounts of sulphate adsorbed by soils vary widely, depending on the type of soil and genetic horizon. In Podzols, the highest sulphate contents as well as sulphate adsorption capacity are normally found in the spodic (Podzolic) horizon (Nommik et al. 1984).

Various studies have demonstrated the close relationship between the soil content of free iron and aluminum oxides and their sulphate adsorption capacity (e.g., Johnson and Todd 1983). Moreover, sulphate adsorption capacity is positively related to the content of 1:1 clay minerals (e.g., kaolinite) whereas organic matter may exert a blocking effect on soil sulphate adsorption sites (Johnson et al. 1979).

An important consideration from the cation leaching point of view is that the mechanism of specific adsorption of sulphate can buffer the chemical effects of  $H_2SO_4$  and create new cation exchange sites. Thus, it is generally found that cation leaching is reduced as long as sulphate is retained, since there are either no anions to accompany the cations moving through the soil, or sulphate mediates a release of  $OH^-$  from other surfaces of iron and aluminum oxides and 1:1 clay minerals, neutralizing the protons introduced into the system with  $H_2SO_4$ . At some point the sulphate retention capacity of the soil will be exceeded and the leaching of cations will increase (Johnson and Cole 1980). Thus, sulphate retention may be considered as a mechanism that delays the response of watershed systems to inputs of acid deposition (Nommik et al. 1988).

The objective of the work reported herein is to determine whether soils in Alberta have the capacity to adsorb sulphate as reported in the studies indicated above. The study focussed on surface horizons of forest soils, some of which are classified as Podzolic B horizons, but included all soils in the Long Term Monitoring Study of Alberta Environment, two of which were within the Chernozemic order of soils.

### 2.3.2 Materials and Methods

Soil samples (LFH and mineral horizons) were either obtained from archived samples of the eight Alberta Environment (AE) acid deposition monitoring sites or sampled (5 sites) by ARC and AE staff during the summer and fall of 1991. Selected chemical data for all 13 sites are reported



in Section 6 of this report. The Alberta Environment acid deposition monitoring sites used were: Bruderheim, Cold Lake, Devon, Esther, Ft. McMurray 2, High Prairie, Rocky Mountain House and Twin Butte. The other five sites sampled by ARC and AE staff were: Edson, Hinton 1, Hinton 2, Peers and the ADP field plots at Ft. McMurray (Ft. McMurray 1).

Sulphate adsorption isotherms were determined for the LFH (except for the Esther site) and one composite mineral soil sample from all 13 sites. The mineral composite samples were obtained by combining the mineral soil horizons down to 30 cm with the contribution of each horizon proportional to its depth.

Sulphate adsorption isotherms were obtained using a modification of the USEPA method 13 for sulphate adsorption measurements (Cappo et al. 1987). The modification included the use of 5 g of mineral soil material and 2 g of LFH samples suspended in 25 mL of the sulphate solution (0, 6, 12, 24, 48 and 96 mg L<sup>-1</sup>). The soil-solution mixtures (triplicates of each sample) were shaken for 1 hr in capped polypropylene centrifuge tubes and later centrifuged at 22 000 xg for 10 min in a Beckman J2-21 centrifuge equipped with a 14 x 50 mL fixed angle head rotor. The supernatants were filtered through Whatman #2 filters and then through Millipore 0.45 µm filters prior to analysis.

Sulphates were measured before and after the adsorption experiment using ion chromatography with a Waters HPLC system and the following equipment and conditions:

- A Waters IC-Pak anion column (4.6x50 mm) with an IC-Pak anion guard column. A borate/gluconate eluant was used at 1.2 mL/min and 750 psi.
- A Waters 712 WISP autosampler.
- A Waters model 430 conductivity detector.
- A Waters MAXIMA 820 chromatography workstation.

Calculations of the adsorbed sulphates (mg g<sup>-1</sup>) were done as follows:

$$\text{Ads. SO}_4 = \frac{(\text{Added SO}_4 - \text{Found SO}_4)(\text{mg L}^{-1}) \times \text{Volume (0.025 L)}}{\text{Sample Weight (g)}},$$

where both Added and Found sulphates were measured by ion chromatography as discussed above.

### 2.3.3 Results and Discussion

The mean (3 replicates) data for sulphate adsorption in both LFH and mineral soil samples from the 13 sites are shown in Table 1 and in Table 8, Appendix 8.1. The data show that the adsorption of sulphate was not evident for all the 13 sites studied. The Hinton 2 site was the only soil that exhibited any, albeit very small, adsorption and only at higher  $\text{SO}_4^{2-}$  concentrations (Table 1).

All 13 sites exhibited a tendency to desorb sulphate at most added  $\text{SO}_4^{2-}$  concentrations. When no sulphates were added, the highest desorbed concentrations (25 mg/L) were for the Edson site, and the lowest (4.9 mg/L) were for the Esther soil.

The above data show that the adsorption of sulphates is negligible for the Alberta soils studied. This effect is due either to the fact that these soils do not contain the required minerals for adsorption (Johnson and Todd 1983), or to a possibility that these soils have already been fully sorbed with sulphates (Nommik et al. 1988). The assumption of negligible soil adsorption of sulphates used in the ARC model is thus valid. The implications of this data are that acid inputs (in sulphate form) are not buffered by adsorption in our soils and thereby could contribute to cation leaching.

Further investigation of the individual horizons of the Hinton and Edson sites would likely reveal higher adsorption in the Podzolic B horizons if compositing were eliminated and these horizons were considered individually.



Table 1. Mean data for the adsorption of  $\text{SO}_4^{2-}$ .

Site	Sample Type	$\text{SO}_4^{2-}$ (added) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (found) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (Adsorbed) (mg g <sup>-1</sup> )	
				mean	sd
Ft. McMurray 1	LFH	0.0	7.3	-0.09	0.011
Ft. McMurray 1	LFH	6.4	13.2	-0.09	0.009
Ft. McMurray 1	LFH	11.2	19.6	-0.10	0.006
Ft. McMurray 1	LFH	24.9	31.6	-0.08	0.005
Ft. McMurray 1	LFH	48.8	57.4	-0.11	0.016
Ft. McMurray 1	LFH	95.4	106.4	-0.14	0.017
Ft. McMurray 1	Composite	0.0	5.6	-0.03	0.001
Ft. McMurray 1	Composite	6.5	11.6	-0.03	0.001
Ft. McMurray 1	Composite	12.5	16.7	-0.02	0.002
Ft. McMurray 1	Composite	23.9	29.0	-0.03	0.002
Ft. McMurray 1	Composite	47.7	52.9	-0.03	0.001
Ft. McMurray 1	Composite	95.4	102.4	-0.04	0.010
Bruderheim	LFH	0.0	16.6	-0.21	0.010
Bruderheim	LFH	5.6	23.5	-0.22	0.004
Bruderheim	LFH	12.6	29.6	-0.21	0.004
Bruderheim	LFH	24.2	41.2	-0.21	0.019
Bruderheim	LFH	46.7	64.0	-0.22	0.004
Bruderheim	LFH	99.5	107.0	-0.09	0.010
Bruderheim	Composite	0.0	6.7	-0.03	0.001
Bruderheim	Composite	6.3	12.2	-0.03	0.000
Bruderheim	Composite	11.8	17.7	-0.03	0.002
Bruderheim	Composite	23.1	28.6	-0.03	0.002
Bruderheim	Composite	46.7	59.1	-0.06	0.004
Bruderheim	Composite	94.8	100.4	-0.03	0.002
Cold Lake	LFH	0.0	14.0	-0.17	0.002
Cold Lake	LFH	6.1	18.7	-0.16	0.010
Cold Lake	LFH	11.7	27.3	-0.20	0.004
Cold Lake	LFH	23.7	38.5	-0.19	0.006
Cold Lake	LFH	46.6	60.4	-0.17	0.013
Cold Lake	LFH	99.0	115.4	-0.20	0.086
Cold Lake	Composite	0.0	5.2	-0.02	0.001
Cold Lake	Composite	6.3	10.3	-0.02	0.003
Cold Lake	Composite	12.1	15.9	-0.02	0.007
Cold Lake	Composite	24.7	28.6	-0.02	0.005
Cold Lake	Composite	47.6	52.5	-0.02	0.003
Cold Lake	Composite	96.3	100.4	-0.02	0.004

continued . . .

Table 1. Continued.

Site	Sample Type	$\text{SO}_4^{2-}$ (added) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (found) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (Adsorbed) (mg g <sup>-1</sup> )	
				mean	sd
Devon	LFH	0.0	15.7	-0.20	0.006
Devon	LFH	6.1	22.3	-0.20	0.010
Devon	LFH	11.7	28.9	-0.21	0.000
Devon	LFH	23.7	39.9	-0.20	0.008
Devon	LFH	46.6	60.0	-0.17	0.015
Devon	LFH	99.0	120.2	-0.26	0.011
Devon	Composite	0.0	6.7	-0.03	0.002
Devon	Composite	6.3	13.1	-0.03	0.003
Devon	Composite	12.1	18.5	-0.03	0.004
Devon	Composite	24.7	30.3	-0.03	0.007
Devon	Composite	47.6	54.3	-0.03	0.005
Devon	Composite	96.3	101.9	-0.03	0.003
Edson	LFH	0.0	25.4	-0.32	0.003
Edson	LFH	6.4	33.2	-0.34	0.002
Edson	LFH	11.2	38.2	-0.34	0.023
Edson	LFH	24.9	53.7	-0.36	0.017
Edson	LFH	48.8	75.9	-0.34	0.067
Edson	LFH	95.4	131.8	-0.45	0.054
Edson	Composite	0.0	6.7	-0.03	0.000
Edson	Composite	5.6	12.4	-0.03	0.001
Edson	Composite	12.1	17.1	-0.02	0.003
Edson	Composite	23.7	28.9	-0.03	0.004
Edson	Composite	45.7	52.5	-0.03	0.002
Edson	Composite	95.5	97.6	-0.01	0.003
Ft. McMurray 2	LFH	0.0	13.4	-0.17	0.006
Ft. McMurray 2	LFH	6.4	18.9	-0.16	0.006
Ft. McMurray 2	LFH	11.2	26.0	-0.18	0.003
Ft. McMurray 2	LFH	24.9	38.9	-0.17	0.003
Ft. McMurray 2	LFH	48.8	64.5	-0.20	0.001
Ft. McMurray 2	LFH	95.4	111.3	-0.20	0.033
Ft. McMurray 2	Composite	0.0	4.7	-0.03	0.006
Ft. McMurray 2	Composite	6.5	11.2	-0.02	0.004
Ft. McMurray 2	Composite	12.5	15.7	-0.01	0.004
Ft. McMurray 2	Composite	23.9	28.4	-0.02	0.002
Ft. McMurray 2	Composite	47.7	51.0	-0.02	0.001
Ft. McMurray 2	Composite	95.4	100.1	-0.02	0.006

continued . . .

Table 1. Continued.

Site	Sample Type	$\text{SO}_4^{=}$ (added) (mg L <sup>-1</sup> )	$\text{SO}_4^{=}$ (found) (mg L <sup>-1</sup> )	$\text{SO}_4^{=}$ (Adsorbed) (mg g <sup>-1</sup> )	
				mean	sd
High Prairie	LFH	0.0	12.8	-0.16	0.028
High Prairie	LFH	5.6	19.7	-0.18	0.021
High Prairie	LFH	12.6	27.1	-0.18	0.005
High Prairie	LFH	24.2	38.0	-0.17	0.001
High Prairie	LFH	46.7	62.0	-0.19	0.008
High Prairie	LFH	99.5	104.5	-0.06	0.059
High Prairie	Composite	0.0	6.0	-0.03	0.001
High Prairie	Composite	6.3	11.0	-0.02	0.002
High Prairie	Composite	11.8	16.7	-0.02	0.002
High Prairie	Composite	23.1	27.0	-0.02	0.003
High Prairie	Composite	46.7	50.6	-0.02	0.002
High Prairie	Composite	94.8	99.2	-0.02	0.012
Hinton Site 1	LFH	0.0	16.1	-0.20	0.009
Hinton Site 1	LFH	6.1	22.8	-0.21	0.014
Hinton Site 1	LFH	12.0	28.5	-0.21	0.005
Hinton Site 1	LFH	24.2	40.9	-0.21	0.027
Hinton Site 1	LFH	47.3	64.9	-0.22	0.007
Hinton Site 1	LFH	94.4	108.1	-0.17	0.036
Hinton Site 1	Composite	0.0	6.3	-0.03	0.000
Hinton Site 1	Composite	5.6	11.6	-0.03	0.001
Hinton Site 1	Composite	12.1	16.9	-0.02	0.003
Hinton Site 1	Composite	23.7	28.8	-0.03	0.001
Hinton Site 1	Composite	45.7	50.3	-0.02	0.001
Hinton Site 1	Composite	95.5	97.0	-0.01	0.004
Hinton Site 2	LFH	0.0	10.1	-0.13	0.012
Hinton Site 2	LFH	6.1	17.5	-0.14	0.020
Hinton Site 2	LFH	12.0	22.2	-0.13	0.011
Hinton Site 2	LFH	24.2	37.4	-0.16	0.018
Hinton Site 2	LFH	47.3	61.2	-0.17	0.016
Hinton Site 2	LFH	94.4	104.1	-0.12	0.013
Hinton Site 2	Composite	0.0	4.5	-0.02	0.001
Hinton Site 2	Composite	5.9	8.0	-0.01	0.001
Hinton Site 2	Composite	11.9	13.3	-0.01	0.003
Hinton Site 2	Composite	23.9	23.1	0.00	0.003
Hinton Site 2	Composite	48.1	44.9	0.02	0.003
Hinton Site 2	Composite	97.1	91.5	0.03	0.002

continued . . .

Table 1. Concluded.

Site	Sample Type	$\text{SO}_4^{2-}$ (added) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (found) (mg L <sup>-1</sup> )	$\text{SO}_4^{2-}$ (Adsorbed) (mg g <sup>-1</sup> )	
				mean	sd
Rocky Mtn. House	LFH	0.0	14.0	-0.18	0.013
Rocky Mtn. House	LFH	5.6	21.0	-0.19	0.010
Rocky Mtn. House	LFH	12.6	26.3	-0.17	0.014
Rocky Mtn. House	LFH	24.2	37.1	-0.16	0.023
Rocky Mtn. House	LFH	46.7	60.3	-0.17	0.015
Rocky Mtn. House	LFH	99.5	102.2	-0.03	0.035
Rocky Mtn. House	Composite	0.0	7.0	-0.04	0.002
Rocky Mtn. House	Composite	6.3	14.0	-0.04	0.009
Rocky Mtn. House	Composite	11.8	18.6	-0.03	0.005
Rocky Mtn. House	Composite	23.1	28.7	-0.03	0.001
Rocky Mtn. House	Composite	46.7	55.3	-0.04	0.004
Rocky Mtn. House	Composite	94.8	102.3	-0.04	0.003
Twin Butte	LFH	0.0	18.7	-0.23	0.007
Twin Butte	LFH	6.1	25.2	-0.24	0.010
Twin Butte	LFH	11.7	32.1	-0.26	0.020
Twin Butte	LFH	23.7	45.7	-0.28	0.007
Twin Butte	LFH	46.6	66.1	-0.24	0.028
Twin Butte	LFH	99.0	125.1	-0.33	0.047
Twin Butte	Composite	0.0	9.2	-0.04	0.006
Twin Butte	Composite	6.3	14.0	-0.03	0.008
Twin Butte	Composite	12.1	20.1	-0.04	0.005
Twin Butte	Composite	24.7	32.1	-0.04	0.002
Twin Butte	Composite	47.6	58.3	-0.05	0.004
Twin Butte	Composite	96.3	105.8	-0.05	0.003
Peers	LFH	0.0	16.5	-0.21	0.006
Peers	LFH	6.1	23.0	-0.21	0.010
Peers	LFH	12.0	26.8	-0.19	0.054
Peers	LFH	24.2	38.2	-0.18	0.009
Peers	LFH	47.3	57.9	-0.13	0.034
Peers	LFH	94.4	108.0	-0.17	0.028
Peers	Composite	0.0	6.2	-0.03	0.002
Peers	Composite	5.6	12.2	-0.03	0.003
Peers	Composite	12.1	17.1	-0.03	0.003
Peers	Composite	23.7	28.9	-0.03	0.002
Peers	Composite	45.7	51.9	-0.03	0.002
Peers	Composite	95.5	100.5	-0.02	0.006
Esther	Composite	0.0	4.9	-0.03	0.002
Esther	Composite	6.5	10.9	-0.02	0.001
Esther	Composite	12.5	16.3	-0.02	0.002
Esther	Composite	23.9	28.8	-0.03	0.005
Esther	Composite	47.7	52.5	-0.02	0.003
Esther	Composite	95.4	102.5	-0.03	0.006



### 3. ORGANIC SOIL COMPONENT

#### 3.1 INTRODUCTION

The purpose of the organic component of this project is to acquire a knowledge and data base of organic soil properties and processes in order to enhance the performance of a predictive model of acid deposition impacts on soils. It is necessary to further divide the organic soil component into two parts, namely the organic material associated with upland mineral soils (the forest floor, or litter, or duff layer of forest soils) and the material constituting organic soils of peatlands. The effect of organic materials associated with mineral soils has not been evaluated in previous modelling assessments of acid deposition impacts (Turchenek and Abboud 1988). Models for evaluation of acid deposition impacts on peatland soils have not yet been developed. The approach taken in this initial appraisal of these soil materials is to review the recent literature on acid deposition impacts, and to develop a conceptual model of acid deposition impacts which would guide further work on laboratory or field studies and on modelling efforts.

#### 3.2 NATURE OF SOIL ORGANIC MATERIALS

Soil organic materials consist of live organisms and their undecomposed, partly decomposed, and completely transformed remains. Soil organic matter is the term usually applied more specifically to the non-living material which is a heterogeneous mixture of products resulting from microbiological and chemical transformations of organic remains. Materials recognizable as plant components are termed 'plant debris'. Substances in which cellular organization of plant material is no longer present are referred to as 'humus'. Humus includes humic substances which are differentiated on the basis of pH dependent solubility into humic, fulvic and humin fractions, and non-humic substances which are compounds belonging to recognizable classes such as carbohydrates, proteins, lipids, and organic acids (Stevenson 1982). The physical and chemical forms of organic matter differ among soils. A number of major kinds of organic horizons in soils are widely recognized (Buol et al. 1980). The following are types pertinent to soils in Alberta:

1. Organic matter of Chernozemic soils and surface layers of cultivated soils; along with the organo-mineral horizons of deciduous forest soils, this type is commonly referred to as 'mull';
2. The LFH layers, in different combinations, of forest soils; this type is equivalent to 'mor' as described by Buol et al. (1980);



3. Organic matter of Solonchic B horizons, which occurs as dark coatings on the surfaces of soil structural units;
4. Organic matter of Podzolic B horizons occurring as dark reddish brown to black, soft, weakly granular layers; these are relatively uncommon in Alberta; and,
5. Organic matter of the Organic order of soils, or peat soils, which occurs in various degrees of decomposition.

Each of these has unique characteristics that will influence the effects of acid deposition on soils in different ways. The following sections focus on organic materials that are not intimately associated with the mineral component of soils, namely the organic matter of forest floors and of peat soils.

### 3.3 ORGANIC MATTER OF FOREST FLOORS

Organic matter is a soil component that includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil microbial and microfaunal population (Canadian Society of Soil Science 1976). In forest soils, the term 'forest floor' refers to all dead organic matter including litter and unincorporated humus of the mineral soil surface. Litter consists of the surface additions of freshly fallen leaves, twigs, stems, bark and other vegetative components (Armson 1977).

Humus is the fraction of organic matter that remains after most of the added plant and animal residues have decomposed. It is usually dark coloured (Canadian Society of Soil Science 1976). The forest floor consists of organic material in various stages of decomposition, and the decomposition stage is the basis for categorizing these materials into one of three types, as follows (Canadian Society of Soil Science 1976):

1. L Layer - organic residues of leaves, twigs, woody residues and mosses in which the original structures are easily recognized.
2. F layer - organic residues (as above) that are partly decomposed.
3. H layer - organic residues decomposed to the extent that the original structures are unrecognizable.

The uppermost mineral soil horizon is the A; when this layer consists of an intimate mixture of well decomposed organic matter and mineral soil, it is referred to as an Ah horizon. In some soils, a mechanical mixing of H material and mineral soil can be distinguished as an Ah horizon. Forest soils usually have Ae horizons which are characterized by relatively light colours due to

removal (by eluviation) of clay, iron, aluminum, or organic matter alone or in combination with each other. Mineral horizons with some organic matter incorporation along with evidence of eluviation are Ahe horizons.

The forest floor can consist of different proportions of the above layers, which are referred to as 'forest humus forms'. Three main forms are commonly distinguished.

The mor forest humus form consists of litter (L) material overlying a matted layer of partly decomposed (F) material in which the degree of decomposition increases with depth. Yellow and white strands of fungal mycelia are often visible in the F layer. The F layer grades into a lower horizon of well decomposed (H) material. This material shows an abrupt transition to the underlying A horizon. In forest soils of Alberta, little or no H material is present and the L-F-H layer overlies a strongly bleached Ae horizon.

A moder humus form consists of litter (L) material overlying F material. H material is mixed into the A horizon and may form either an Ah or Ahe horizon. Forest soils transitional to grassland soils on the prairies commonly have this horizon sequence.

In soils with mull surface layers, litter (L) material may be present but it decomposes rapidly over the growing season. The uppermost soil layer is an Ah horizon. Such forest floors are typical of deciduous forests in relatively milder and moisture climates as compared to boreal forest climates in Alberta. This humus form, however, is typical of grassland soils.

The forest floors of the northern boreal and foothills soils of Alberta, as noted above, are typified by the mor humus form. Mors are characterized by high carbon contents, high C/N ratios, and high cation exchange capacities as compared to mineral soil materials. As decomposition rates of mors are low, nutrients are likewise slowly released and made available to plants. Mors can occur under different moisture regimes ranging from well aerated, terrestrial forms that can be temporarily saturated to poorly aerated, terrestrial to semi-terrestrial forms influenced by prolonged or permanent saturation (Klinka et al. 1981). In the latter case, these materials are transitional to peat and are categorized as peat if the thickness exceeds 40 cm. For purposes of addressing the influence of acidic deposition on forest floor materials, only the well drained and aerated type described above will be considered. Poorly drained and aerated organic materials will be considered as peat materials. Consequently, some properties that influence soil acidity, such as oxidation-reduction, will have more relevance to peat materials than to forest floor materials.

### 3.4 ORGANIC MATTER OF PEAT SOILS

Peatlands are abundant in Alberta, having an estimated area of 12.7 million hectares or about 19% of the land area of the province (Turchenek 1990). They occur in the central and northern portions of the province, and are highly variable in their properties, ranging from shallow deposits of peat associated with sloughs and potholes in the parkland regions to deep deposits with permafrost in the subarctic regions of the north.

#### 3.4.1 Terminology and Definitions

Peatlands are unbalanced systems in which the rate of production of organic materials by living organisms exceeds the rate of decomposition, usually under conditions of almost continuous saturation by water. The result is an accumulation of an organic deposit which is termed 'peat'. As a peat deposit thickens, the surface vegetation becomes isolated from underlying soils and rocks, and the resulting environmental changes are often accompanied by floristic changes that reflect the altered hydrology and chemistry of the peat surface (Moore and Bellamy 1974). The chemical composition of peat is influenced by the nature of the plants from which it has originated and by the moisture conditions during and following its formation and accumulation.

Various definitions for peat can be found in the literature with variations arising due to origins in different scientific and applied disciplines. For purposes of forest science technology, Ford-Robertson (1971) defined peat as unconsolidated material consisting largely of undecomposed, or only slightly decomposed, organic matter accumulated under conditions of excessive moisture. The definition of the Canadian Society of Soil Science (1976) is similar except that peat is referred to as a soil material. Definitions developed by the International Peat Society, as reported by Stanek and Worley (1983), represent an attempt to standardize certain peat and peatland terms internationally. The definition of peat from this source is as follows:

**Peat** -material constituting peatlands, exclusive of the live plant cover, consisting largely of organic residues accumulated as a result of incomplete decomposition of dead plant constituents under conditions of excessive moisture (submergence in water and/or waterlogging).

Peat may contain a variable proportion of transported mineral material; it may form in both base-poor and base-rich conditions; it is usually formed in situ, but can also be a transported and redeposited material; and it may contain basal layers of coprogenic elements and comminuted plant remains or humus gels. The physical and chemical properties of peat are influenced by the nature of



the plants from which it has originated, by the moisture relations during and following its formation and accumulation, by geomorphological position, and by climatic factors. The moisture content of peat is usually high; the maximum water-holding capacity occurs in Sphagnum peat, being over 10 times its dry weight and over 95% of its volume. Most peats have a high organic content (85% and more). However, in general, peat must have an organic matter content of not less than 30% of the dry weight (Stanek and Worley 1983).

The criteria for organic matter content in the definition above (i.e., more than 30% organic matter) are the same as for definitions of Organic soils or Organic soil horizons in the Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Survey 1987), and for the Histosol order in the system used in the USA. The description of Organic soil from Stanek and Worley (1983) is as follows:

**Organic soil** - term used in the Canadian and U.S. soil classifications for soils that have developed primarily from plant remains and contain >30% of organic matter (17% or more carbon derived from the organic matter). They are classified on the basis of decomposition, type of plant fibers, and presence of mineral, frozen, water or rock layers.

The definition for peatland from the National Wetlands Working Group (1988) is as follows:

**Peatland** - a generic term including all types of peat-covered terrain.

Depth of peat, with 20 to 40 cm being a common limit, has been used as a criterion for distinguishing peatlands from mineral soils (Jeglum et al. 1974; Stanek and Worley 1983). In Canada, depth criteria for the Organic order in the Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Survey 1987) are generally applied. This depth is 40 cm or more where peat overlies unconsolidated materials, or 10 cm or more where it overlies rock.

Terms such as bog, swamp, muskeg, and marsh have general layman's usage as well as more restricted technical meanings (Jeglum et al. 1974). Of these, bog, marsh, and swamp are used in a restricted sense and, along with the terms 'fen' and 'shallow water', are used for the main wetland classes in the Canadian Wetland Classification System (National Wetlands Working Group 1987, 1988). Two of these classes are categorized as peatlands, while swamps can have either mineral or peat substrates. A bog is a peatland that receives its nutrients solely from precipitation. It is generally acidic, low in nutrients and has a water table at or near the surface. The bog surface may be level or raised. The peat in bogs is usually at a mild to moderate state of decomposition. Vegetation of bogs

consists chiefly of Sphagnum mosses and ericaceous shrubs. Fens receive richer nutrient supplies than bogs from runoff and groundwater sources. Fens are less acidic than bogs, and their vegetation consists mainly of sedges, reeds, grasses, brown mosses, shrubs and trees such as tamarack. The peat in fens is generally more strongly decomposed than that in bogs. The water table is generally at or near the surface. Swamps are mineral wetlands or peatlands with standing or gently flowing waters in pools and channels. If peat is present, it is mainly well decomposed wood peat underlain at times by sedge peat. The vegetation cover is normally a dense cover of trees and shrubs. The water table is usually at or near the surface.

Peatlands can also be categorized on the basis of the contents of nutrients and dissolved ions in peatland waters. The categories of bog, poor fen, transitional rich fen, and extreme rich fen have been applied in Alberta. Characteristics of these are presented in Table 2.

### 3.4.2 Peatland Soil, Water and Landscape Factors in Acidification

A peat deposit, or Organic soil, consists of about 10 percent organic matter and 90 percent ambient water when considered on a volumetric basis instead of a weight basis. Consequently, peat soils should probably be thought of as organic matrix-ambient water systems (Holowaychuk et al. 1987). Because of their constitution and hydrology, peat soils as terrain components are transitional between terrestrial and aquatic systems. A definition of acidification of peatlands is, therefore, more complex than that of soil or water only. Reuss and Johnson (1986) indicated that the term acidification as applied to soil systems refers to a complex set of processes. Holowaychuk et al. (1987) have considered sensitivity of soils to acidification mainly in terms of exchangeable base loss, reduction in pH and solubilization of Al. The acidification of lakes and streams (surface waters) is defined in terms of decrease in alkalinity over time. The assessment of sensitivity of lakes in Alberta to acidification has been based on levels of alkalinity,  $\text{Ca}^{++}$ , pH and total dissolved solids (Erickson and Trew 1986). The acidification of Organic soils needs to be considered in terms of processes occurring in both soil and aquatic systems, and probably most importantly in terms of base loss and decrease in alkalinity. Waters with alkalinity of 0-10 mg L<sup>-1</sup>, or about 164 mmole(HCO<sub>3</sub>)L<sup>-1</sup>, are considered to be highly sensitive to acidification in Alberta (Erickson and Trew 1987). Soils of cation exchange capacity <6.0 cmole(+)kg<sup>-1</sup> and pH <6.5 are considered to have a low total base content and are therefore highly sensitive to base loss (Holowaychuk et al. 1986). Oligotrophic and mesotrophic peatlands have a much lower cation exchange capacity than most



Table 2. Water chemistry variation and vegetation characteristics in Alberta peatlands.<sup>1</sup>

	Bog	Poor Fen	Transitional Rich Fen	Extreme Rich Fen
Ca <sup>++</sup> mg L <sup>-1</sup>	0-2	0-5	0-40	30-85
Mg <sup>++</sup> mg L <sup>-1</sup>	0-1	0-2	1-8	2-34
Na <sup>+</sup> mg L <sup>-1</sup>	1-2	1-2	1-20	1-20
K <sup>+</sup> mg L <sup>-1</sup>	0-1	0-1	0-3	1-4
pH	3.5-3.9	4.0-5.5	(5.5) 6.0-7.2	7.3-7.8
Reduced conductivity μS cm <sup>-1</sup>	0-20	0-95	14 -120	235-490
Alkalinity mg L <sup>-1</sup> CaCO <sub>3</sub>	0	0-4	4-40	>40
TKN μg L <sup>-1</sup>	900-2000	730-1900	1600-3000	920-1700
NO <sub>3</sub> μg L <sup>-1</sup>	3-14	0-17	0-16	0-62
NH <sub>3</sub> μg L <sup>-1</sup>	10-47		1-37	0-1180-77
P mg L <sup>-1</sup>	0-1	0-1	0-1	0-1
Species diversity (no. species)				
Sphagnum	3-8	4-10	2-3	0-1
brown mosses	few			many
vascular plants	few (5-10)			many (20-30)

<sup>1</sup>Adapted from Nicholson (1990) and Rochefort (1990).

mineral soils if the comparison is made on a volumetric basis. Since these peatlands are characterized by low pH, alkalinity and buffering capacity are also very low. However, various other factors need to be considered in peatland acidification and in ultimate influences of acid deposition on surface waters.

#### 3.4.3 Hypothesized Controls on Peatland and Water Acidification

The acidity budget of peatlands is determined by several complex biogeochemical factors including nutrient uptake by plants, decomposition of vegetation, redox reactions, cation and anion exchange with the peat, rock and soil weathering and inputs of alkalinity (Gorham et al. 1987). These are described with examples in Table 3.

The acidic nature of peatland waters originates from three major sources: (1) organic acids (fulvic and humic acids) produced from decomposition within the peatland itself, (2) mineral acids (e.g. sulphuric and nitric acid) from atmospheric deposition of sulphates and nitrates derived from anthropogenic and/or natural sources, as well as mineral acids (e.g. carbonic acid) formed by the decomposition of organic matter, and (3) biological uptake of cations and exchange by the soil. Gorham et al. (1985) have noted that there has been a long-standing controversy as to whether the free hydrogen ions in bog waters can be attributed to organic acids, sulphuric acid, or to cation exchange between metallic cations in precipitation and hydrogen ions adsorbed by the polygalacturonic acids that make up the cell walls in Sphagnum moss and peat. Recent studies of peatlands in North America, England and Ireland generally indicate that organic acids (chiefly humic and fulvic acid) are the dominant source of acidity in most peatlands and, therefore, have a major effect on the acidity budget (Gorham et al. 1985). However, there appears to be evidence that the ongoing regional acidification of surface waters is not caused by organic acids (Brakke et al. 1988; Eilers et al. 1988). Mineral acids appear to be a dominant source of acidity in severely polluted peatlands in England and near point sources in North America such as Sudbury, Ontario where atmospheric deposition of sulphates is extremely high (Glooschenko and Stevens 1986; Gorham et al. 1985; Gorham and Detenbeck 1986).

Dissolved organic carbon plays an important role in the acidity balance of receiving waters because it may acidify and/or buffer the waters emanating from wetlands, reduce metal toxicity (particularly aluminum), alter the cycling of metals and decrease the primary productivity of water by

Table 3. Summary of proton producing and consuming processes.<sup>1</sup>

Proton-producing processes (Proton-consuming processes)	Examples
(1) Atmospheric input (Drainage)	$H^+ (aq(rain/drain\ water)) =$ $H^+ (aq(soil\ solution))$
(2) Assimilation of cations (Mineralization of cations)	$M^+ + R_{OH} = R_{OM} + H^+$  $M^+ + H.Ligand = M.Ligand + H^+$  $NH_4^+ + R.OH = R.NH_2 + H_2O + H^+$  where source may be;  $Biomass(Nb) + aO_2 = aCO_2 + bNH_4^+$
(3) Mineralization of anions (Assimilation of anions)	$R.H_2PO_4 + H_2O = R.OH + H_2PO_4^- + H^+$  $R.SO_4 + 2H_2O = R.(OH)_2 + SO_4^{2-} + 2H^+$  $R.NO_3 + H_2O = R.OH + NO_3^- + H^+$  $R.NH_2 + 2O_2 = R.OH + NO_3^- + H^+$  $R.SH + 3/2 H_2O + 7/4 O_2 =$  $R.OH + SO_4^{2-} + 2H^+$
(4) Dissociation of acids (Protonation of anions)	$H_2O = OH^- + H^+$  $CO_2 + H_2O = HCO_3^- + H^+$  $R.OH = R.O^- + H^+$  $H_n.Anion (aq) = Anion^{n-} (aq) + nH^+$

continued . . .

Table 3. Concluded.

Proton-producing processes (Proton-consuming processes)	Examples
(5) Oxidations (Reductions)	$\text{H}_2\text{S} + 2\text{O}_2 = \text{SO}_4^{2-} + 2\text{H}^+$ $\text{SO}_2 + 1/2 \text{O}_2 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2\text{H}^+$ $\text{NH}_4^+ + 2\text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$ $\text{NO}_x + 1/4 (5-2x)\text{O}_2 + 1/2 \text{H}_2\text{O} = \text{NO}_3^- + \text{H}^+$ $\text{N}_2 + 5/2 \text{O}_2 + \text{H}_2\text{O} = 2\text{NO}_3^- + 2\text{H}^+$ $\text{Fe}^{2+} + 1/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{H}^+$ $\text{FeS} + 9/2 \text{O}_2 + 5/2 \text{H}_2\text{O} =$ $\text{Fe}(\text{OH})_3 + \text{SO}_4^{2-} + 2\text{H}^+$ $\text{FeS}_2 + 15/4 \text{O}_2 + 7/2 \text{H}_2\text{O} =$ $\text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$
(6) Reverse weathering of cations (Weathering of metal oxide components)	$\text{M}^{n+} (\text{aq}) + 1/2n\text{H}_2\text{O} =$ $1/2n\text{M}_{2/n}\text{O}(\text{s}) + n\text{H}^+(\text{aq})$
(7) Weathering of anionic components (Reverse weathering of anions)	$^*\text{NO}_{(m+n)}(\text{S}) + m\text{H}_2\text{O} =$ $\text{NO}_{(2m+n)}^{2m-} + 2m\text{H}^+(\text{aq})$ $\text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{CaHPO}_4 + \text{H}_2\text{PO}_4^- + \text{H}^+$
(8) Cation/hydronium exchange (Hydronium/cation exchange)	$\text{M}^{n+} + n\text{H.Exch} = \text{M.Exch} + n\text{H}^+$
(9) Anion exchange (desorption) (Anion adsorption)	$\text{SO}_4. \text{Exch} + 2\text{H}_2\text{O} =$ $\text{Exch.}(\text{OH})_2 + \text{SO}_4^{2-} + 2\text{H}^+$

<sup>1</sup> Adapted from the original tables in van Breeman et al. (1983, 1984) .

attenuation of light or by diminishing phosphorous and iron availability (Krug and Frink 1983; Gorham et al. 1986). The amount of production of dissolved organic carbon from different wetland types, as well as variability within a single wetland type is not known.

#### 3.4.4 Conceptualizing of Acid Input Effects on Organic Materials

Fens and bogs have markedly different chemical characteristics. Bogs are highly acidic, are low in base cation content, and have unique assemblages of vegetation. Fens on the other hand occur under a comparatively wide range of conditions, from highly acidic to alkaline, from very low to high nutrient status, and so on (see Table 2). Poor fens (Table 2) are regarded as being highly sensitive to acidic deposition due to low buffering capacity. Consequently, conceptualizing of acid deposition effects is best considered in terms of poor fens because of rapid changes that could occur.

The conceptual model of Gorham et al. (1987) also provides an integration of peatland chemical processes along with ecological considerations (Figure 1). As a fen undergoes transition to a bog, minerotrophic inputs are titrated by increasing organic acid inputs from decaying vegetation. Inorganic acid inputs could accelerate this process, and the transition from slightly acidic conditions (pH 5 to 6) to strongly acidic conditions (pH 4) could be quite rapid because the buffering capability is easily exhausted.

The main processes involved in controlling peatland acidity can be summarized from Table 3, the discussion in the previous sections, and from the literature (Anderson 1986; Urban et al. 1987) as follows:

1. Bicarbonate buffering, which would be active in minerotrophic peatlands (pH>5).
2. Ion-exchange and metal complexation reactions.
3. Assimilatory uptake of ions by vegetation.
4. Redox processes at or below the groundwater table; biochemical sulphate and nitrate reduction may be very efficient (e.g., Bayley and Schindler 1987) producing alkalinity. If S compounds are oxidized, an equivalent amount of acidity is produced.
5. Production of organic acids as a result of incomplete aerobic decomposition of organic matter. This acidity arises from the production of fulvic and humic acids which have a high content of carboxylic and phenolic groups.



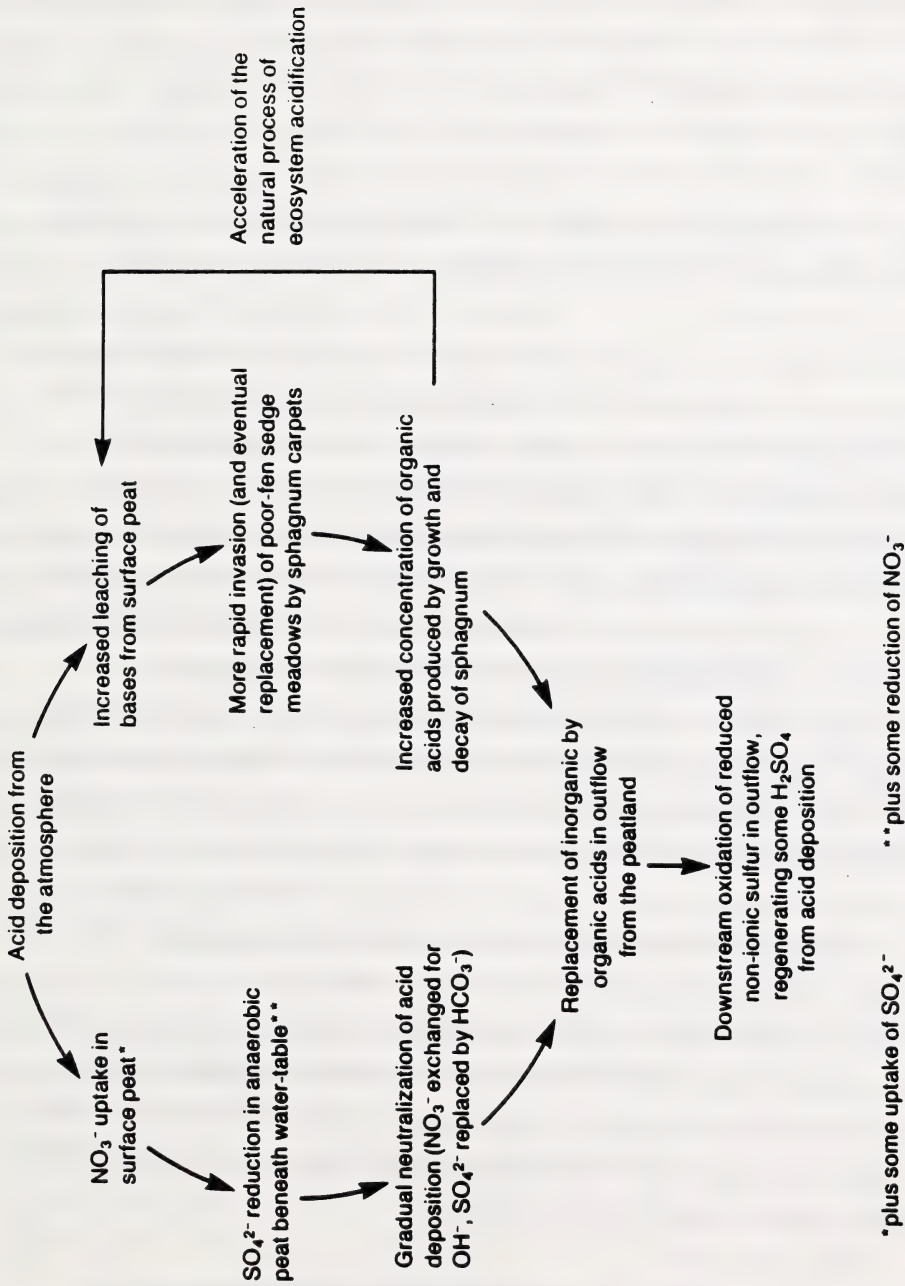
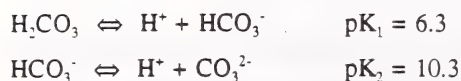


Figure 1. A conceptual model of the chemical and biological effects of acid deposition upon a fen vulnerable to acidification. (Source: Gorham et al. 1987)

Bicarbonate buffering is basically measured by alkalinity whereby inorganic carbon species in water are related by the reactions:



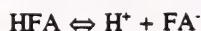
The concentrations of the various species are fixed by the values of  $\text{pK}_1$  and  $\text{pK}_2$ . This can be the main buffering system between pH 5 and 8, and can be significant in peatlands although other mechanisms may also be operative.

Buffering by cation exchange is typically described using cation exchange capacity and base saturation concepts, as for mineral soils. However, there appears to be a continuum of cation - humic substance interactions involving cation exchange as well as various complexation reactions. A quantitative model of complexation by functional groups of humic substances and non-specific ion-exchange reactions was developed by Tipping and Hurley (1988). Relationships between complexed ions and ions in solution are expressed by equations that combine intrinsic equilibrium constants with terms accounting for electrostatic attraction or repulsion between humic binding sites and ions. The model provides simultaneous prediction of solution pH and concentration of  $\text{Al}^{3+}$ .

Assimilatory uptake of ions by vegetation can generate both acidity and alkalinity. Owing to the principal of electroneutrality, charge balance must be maintained between plants and their environment. When a plant takes up cations, other cations (usually  $\text{H}^+$ ) are released into the environment. Similarly, the same mechanism occurs when anions such as hydroxide ( $\text{OH}^-$ ) are produced when anionic nutrients are taken up by plants. In practice, the nutrient ion balance is calculated from the mass budget for a peatland ecosystem as a whole. Such studies have shown net production of acidity (reviewed by Rochefort, 1990, and Wood, 1989).

Redox processes can be important in peatlands, particularly at or below the water table. The redox processes of importance have been listed in Table 3. A conceptual basis for determining oxygen levels and redox potential has been suggested by Clarke-Whistler et al. (1984).

Buffering by organic acids is conceptually similar to bicarbonate (alkalinity) buffering. The general reaction, using fulvic acid (FA) as an example is:



Clarke-Whistler et al. (1984) have suggested an approach to defining buffering intensity that incorporates both alkalinity and organic acid components in peat waters.

There have been no integrated chemical models of peatland response developed to date and the task would be rather challenging due to the complexity of peatland systems. Chemical processes in peatlands are complicated, furthermore, by the control of the hydrologic cycle on various processes and components. The water table in peatlands rises and falls with inputs and outputs of water. The water sources can range from origin completely due to precipitation, to various proportions of precipitation, groundwater and local runoff. Hydrologic controls are especially pertinent to redox processes, and to the sulphur cycle in particular (Wood 1989). A conceptual approach to modelling the hydrologic cycle in peatlands has been described by Clarke-Whistler et al. (1984), but linking hydrology to chemical models still needs to be pursued.

### 3.5 CONCLUSIONS AND RECOMMENDATIONS

Developing an integrated dynamic model of peat soil responses to acid deposition is a large task that is beyond the scope of the ADP soils research program as presently established. Investigation of individual buffering mechanisms is proposed instead, with the conceptual outline of major buffering processes presented in this section providing a mechanism for focussing on relevant processes and on the relationships among processes.

The organic materials of forest floors have not been discussed in terms of buffering mechanisms in this section, but the conceptual model for peat soils is considered to be applicable, at least in part. Major differences in approach stem from differences in drainage regime wherein mechanisms such as reduction and bicarbonate buffering will not be as prominent. Organic matter complexation and biomass assimilation (nutrient cycling effects) are the main processes requiring evaluation and research.

Investigation of buffering in both peat soils and forest floor materials is a component of the proposed second year of soils research within the ADP. Initial activities involve determination of the overall buffering capabilities of organic materials, followed by laboratory examination of the cation exchange and complexation mechanisms of acid buffering.

## 4. MODEL VALIDATION

### 4.1 INTRODUCTION

Confidence in the results provided by predictive models is required for applications such as the derivation of critical loads. Validation of a model is usually carried out by using it to make a prediction about the real-world system and checking the result by direct experimentation or by reference to already-collected data. It is proposed that validation be carried out by experimentation with forest soils as these have been identified as being potentially the most sensitive to acid deposition. The experimental approach entails artificial acidification of field plots using a range of acid input levels, monitoring the effects on soil properties, comparing the results with model predictions, and adjusting the model if necessary. Applying this approach to soils of interest within Alberta is preferred to other possibilities such as use of results from long-term fertilization in agricultural field trials or use of data from other countries or provinces.

### 4.2 ARTIFICIAL ACIDIFICATION OF FIELD PLOTS

#### 4.2.1 Materials and Methods

4.2.1.1 Selection and Location of the Field Site. Criteria for selecting a field site for model validation experiments were as follows:

- 1) The soil needed to be highly susceptible to acid deposition, according to the sensitivity criteria of Holowaychuk and Fessenden (1987). High sensitivity implies a relatively short period of time for measurable acidification impacts to occur in soils, and only such a soil could demonstrate changes within the four year time frame of the project.
- 2) Uniform topography was favoured in order to minimize variability due to slope, aspect and drainage regime.
- 3) Uniform vegetative cover with a minimal understory shrub layer was preferred in order to enable uniform application of acidic solutions to the forest floor.
- 4) Access to a supply of de-ionized water, without the need to haul it long distances, was necessary in order to minimize transportation costs.



- 5) The site required permission of the landowner for use and access, or in the case of crown land, could be reserved for experimental purposes over the time frame of the project.

Sites in the Edmonton, Whitecourt and Ft. McMurray regions were originally considered for potential study sites. Site selection then focussed on the Athabasca oil sands region upon the consent of Syncrude Canada Ltd. to participate in the study. Large areas of sandy soils that are considered to be highly sensitive to acid deposition occur to the east and northeast of the two oil sands processing plants north of Ft. McMurray. Ample supplies of de-ionized water were available at Syncrude Canada Ltd. as well. Several sites were inspected, with access by road or helicopter. Most of the sandy soils in the region were found to be characterized by very low pH and low saturation with exchangeable base cations. It was considered that these kinds of soils could already be too acidic to demonstrate change upon acid treatment. This property seemed to be characteristic of the very sandy soils with very low acid buffering capacity. A soil considered to be suitable for the acidification study was located a short distance south of the Fort Hills, about 6 km south of the Bitumount forestry lookout tower.

The study site is located in LSD5-Sec10-Tp96-R10-W4 Meridian. A location map is presented in Figure 2. It is accessible from Ft. McMurray and Mildred Lake (site of Syncrude Canada Ltd.) via Highway 63 to the Haight Island area, and from there via roads originally constructed for access to the formerly proposed Alsands project area. Driving time out of Ft. McMurray is one to one and one-half hours, and driving time for a water truck from the Syncrude Canada Ltd. plant at Mildred Lake is about one hour.

Use of the site was secured by application for reservation status of the above (legal) location to Alberta Forestry, Lands and Wildlife.

4.2.1.2 Site Description. The soil at the site is an Eluviated Dystric Brunisol developed on coarse to very coarse textured glaciofluvial deposits. The landform is gently undulating. Chemical properties of the soil are included in the table of model inputs in Section 6 (Table 5).

The vegetation at the site consists of a very sparse cover of jack pine (*Pinus banksiana*) with a sparse shrub cover of buffalo berry (*Shepherdia canadensis*). The ground cover consists mainly of bear berry (*Arctostaphylos uva-ursi*) and lichens (*Cladina* spp., *Cladonia* spp.).

The site occurs within the Dry subregion of the Boreal Mixedwood ecoregion as described by Strong and Leggat (1981). This region is characterized by mean summer (May to



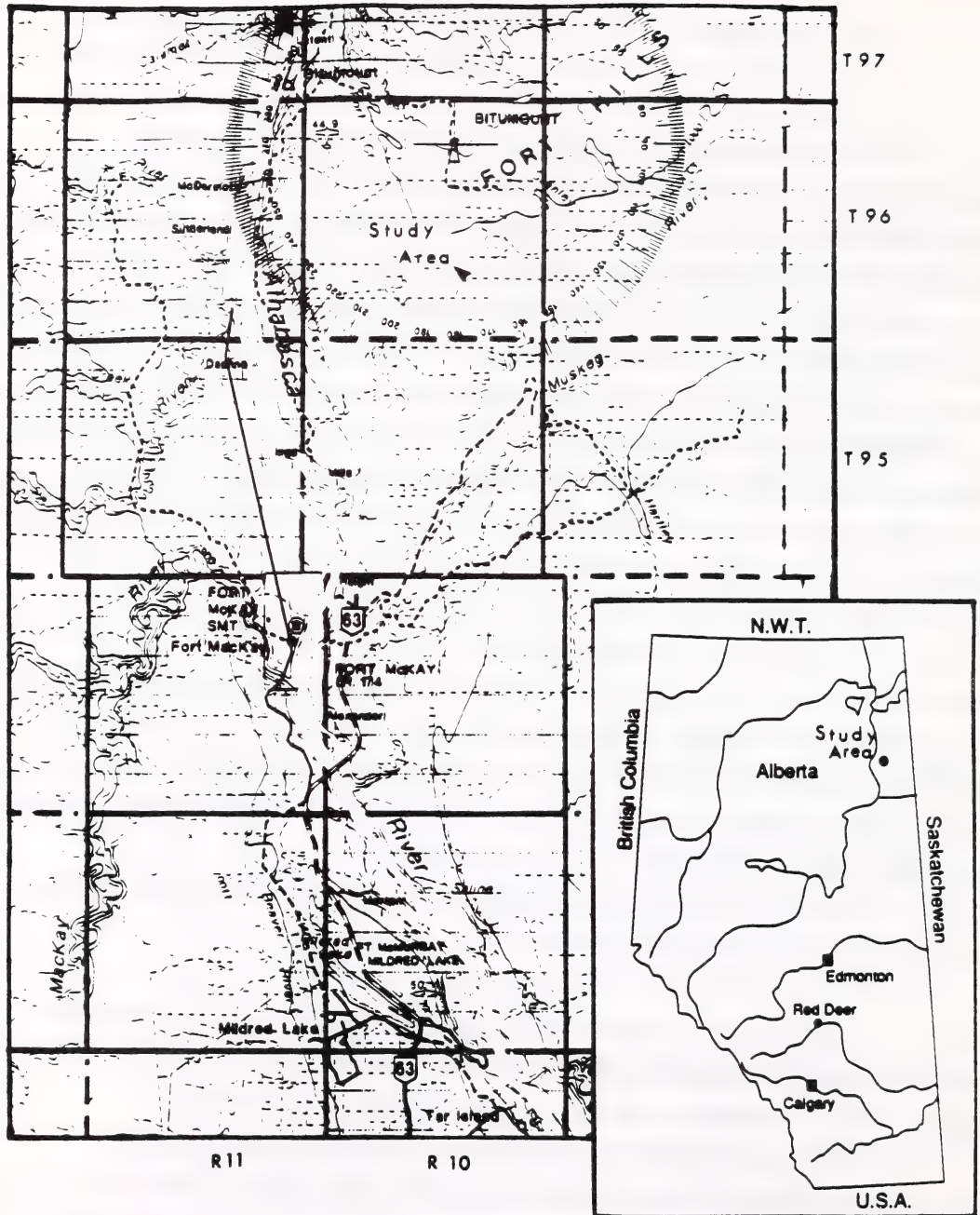


Figure 2. Location of the ADP field site for model validation.

September) precipitation of 200 to 300 mm, October to April precipitation of about 170 mm, mean summer temperatures of about 12°C, and mean winter temperature in the range of -11.5 to -23.5°C.

4.2.1.3 Experimental Design. The experiment was designed for application of 5 levels of acid inputs along with a control. Eighteen plots divided into three blocks were established at the study site. Plot size was determined on the basis of five anticipated sampling events, one prior to treatments of the plots and then one at the end of each of 4 seasons of acid treatment. Prior experience suggested that in order to account for spatial variability in soil properties, each plot sample should be a composite of at least 10 soil probes (or digs) within a plot. Hence, at least 50 potential sampling points within each plot (5 sample events x 10 sample points) were required. A predetermined grid pattern was determined to be an appropriate approach to selecting sampling points, and at least 1 m distance between points was considered to be needed to provide sufficient space for sampling without disturbing adjacent sampling points. A plot size of 10m x 10m = 100 m<sup>2</sup> was initially considered in order to provide ample numbers of sampling points. Logistics of bringing large quantities of water to the site were a consideration that necessitated a smaller plot size. Consequently, a plot size of 8m x 8m = 64 m<sup>2</sup> was selected as being the most suitable. This size permitted a 1 m buffer zone along the perimeter of each plot along with 49 potential sampling points on a 1 m grid. A randomly selected non-grid point would be selected for the 50th sampling point.

The six acid application treatments in the experiment were as follows:

- 1) Control
- 2) 0.3 kmol ha<sup>-1</sup> yr<sup>-1</sup>
- 3) 0.6 kmol ha<sup>-1</sup> yr<sup>-1</sup>
- 4) 1.2 kmol ha<sup>-1</sup> yr<sup>-1</sup>
- 5) 2.4 kmol ha<sup>-1</sup> yr<sup>-1</sup>
- 6) 4.8 kmol ha<sup>-1</sup> yr<sup>-1</sup>

The treatments are based on a minimum level, determined by preliminary modelling, that may have a discernible effect on soil chemistry (Turchenek and Abboud 1988). Intermediate levels are in the area of actual levels reported in the literature. The highest level is considered necessary to provide an adequate range for model validation. The treatments are within the ranges of those reported for similar experiments in Sweden and the USA (e.g., Tamm and Popovic 1989).

4.2.1.4 Plot Establishment and Acid Application. Plots were set out at the study site on July 22-23, 1991. The 8m x 8m plots were measured, staked at the corners, and delineated by stretching nylon cord between the stakes. The cord, when marked at 1 m intervals, also enabled easy location of grid points in subsequent soil sampling activities.

The total amount of acid applied per annum was as indicated in the previous section, and a frequency of application of 3x per annum was selected as operationally optimal. Considerations involving solution pH attained at the highest application rate, as well as logistics of bringing water to a site, suggested that the upper limit of liquid volume per plot should be about 200 liters. A clean water rinse would be required for each plot after acid solution application. A water pre-soak was also suggested as a measure to help reduce the effect of applied acid on the vegetation. An acid application protocol as described below was developed.

1) Pre-soaking

In the AOSERP studies of the late 70s, much data on soil moisture properties, along with other soil characteristics, was collected (McGill et al. 1980). In studies of precipitation infiltration into the soil, it was found that the first 1.5 mm of precipitation was absorbed by the vegetation in sites characterized by sandy soils with jack pine and lichen vegetation. This was found at a few similar sites. It was concluded from this that a 1.5 mm pre-soak would be helpful in preventing the ground vegetation at the experimental site from soaking much of the acid solution applied. For a 64 m<sup>2</sup> area, this corresponded to application of 96 L of water.

2) Acid application

The following summarizes the acid solution requirements for the 64 m<sup>2</sup> plots. An application rate of liquid volume of 2 L m<sup>-1</sup> was selected such that the total applied per plot was 128 L (Table 4). This amount would be applied during each of three acidification events during the growing season.

The solutions described above were pre-measured from concentrated sulphuric acid, taken to the experimental site, and then mixed into 128 L water for plot application. The purity of concentrated acid can vary, as can the resultant concentration of solution mixed for the different acidification events. Therefore, the solutions were titrated with standard base to determine the normality accurately.



Table 4. Acid solution requirements for artificial acidification of field plots.

Treatment kmol ha <sup>-1</sup> yr <sup>-1</sup>	Acid Required per Event	pH of Solution	mL of 10.24N Acid Needed <sup>1</sup>
4.8	10.24 eq 64 m <sup>-2</sup>	~1.1	1000
2.4	5.12 eq 64 m <sup>-2</sup>	~1.4	500
1.2	2.56 eq 64 m <sup>-2</sup>	~1.7	250
0.6	1.28 eq 64 m <sup>-2</sup>	~2.0	125
0.3	0.64 eq 64 m <sup>-2</sup>	~2.3	62.5
0.0	0 eq 64 m <sup>-2</sup>	~6.0	0

<sup>1</sup> Required for dilution to 128 L.

The delivery system for applying acidic solutions to the field plots consisted simply of polyethylene water tanks, polyethylene hose, and a pump. A water tank was set upon an elevated platform (about 2 m high) and a hose was connected to the spigot. A wand constructed from solid plastic was attached to the hose, and a sprinkler head from a plastic watering can was attached to the end of the wand. Water from storage tanks on a truck or on the ground was pumped into the elevated tank. The required amount of acid for each treatment was emptied into the mixing/delivery vat and continued pumping of water into the tank, along with manual mixing with a large stirrer, ensured that mixing to a uniform concentration occurred. The level for obtaining a 128 L volume in the vat was determined in advance and was marked. Acid was mixed by introducing about 1/4 of the water to the vat, adding the concentrated acid, and then adding the rest of the water to the 128 L mark. Samples of the acid mixtures from the delivery tank were taken to measure pH.

A rinse to remove acid solution from plant surfaces was carried out after acid application to the soil. The same volume of water as used for the acid solution application (128 L) was selected for the rinse. Volume considerations included ensuring the amount would be adequate to ensure a complete rinse as well as limiting the total amount of water trucked to the site.

The water used in the above procedures was boiler water obtained from Syncrude Canada Ltd. This is water that has been de-ionized to a relatively high purity level; the electrical conductance is about 1.5 mS cm<sup>-1</sup>.

4.2.1.5 Soil Sampling. The following samples were taken from soils in the plots: LFH layer, 0-5 cm, 5-15 cm, 15-30 cm, 30-50 cm. and 50-80 cm. Sampling was carried out prior to the first application of acidic solutions, and at the end of the growing season.

Samples were taken from 10 different sampling points in each plot, as indicated previously. The sampling points were numbered and a random numbers table was then used to determine which of the 49 sampling points would be used for each sampling event. The top 15 cm of soil was sampled by removing a plug of soil with a square spade. Layers below 15 cm were sampled with a soil auger.

Soil samples were put into plastic bags, transported to the Alberta Research Council laboratories in Edmonton, air dried, and passed through a roller mill to break any aggregates and to separate the fraction <2 mm. The samples from the 10 sampling points within each plot were then composited by measuring equal weights and passing through a sample splitter.

4.2.1.6 Soil Analysis. Soil samples were analyzed at the laboratories of the Soil Protection Branch, Wastes and Chemicals Division, Alberta Environment, Lethbridge. Most analyses were carried out according to the same procedures used on samples from the Long Term Soil Acidification Monitoring Program of Alberta Environment as documented by Roberts et al. (1989). These analyses are: pH ( $\text{CaCl}_2$ ), cation exchange capacity and exchangeable cation determinations by the  $\text{BaCl}_2$  method, extractable acidity, particle size distribution by the pipette method, Al and Fe extracted by sodium pyrophosphate, soluble salts, electrical conductance, extractable N and P, and total C, N and S. Determination of cation exchange capacity and exchangeable cations was also carried out by the ammonium acetate method as described by McKeague et al. (1978). Cation exchange properties were determined by the  $\text{BaCl}_2$  method to conform with the protocol and to enable comparison with the Long Term Soil Acidification Monitoring Program of Alberta Environment. Cation exchange parameters measured by ammonium acetate were required for modelling purposes.

#### 4.3 RESULTS

No results are reported for the artificial acidification experiment at this time. Most of the analyses have been completed and are currently (April 1992) being entered into a data base management system for data reduction and statistical analysis. It is not considered likely that discernible differences in soil chemical properties would have occurred within the first season of acid



application. The data for the first year will be compiled during 1992/93 and compared with soil properties both before application of acid and after the second year of acid additions.

#### 4.4 MODEL SIMULATION OF ACIDIFICATION IN THE PLOT SOIL

In addition to the sampling of soil acidification plots according to the methods outlined above, one soil pit was dug at the site to obtain bulk samples for soil chemistry experiments related to modelling as described in Section 2. The ARC model was used to predict the acidification rate in the artificial acidification experiment. The purpose of the experiment is to verify the model. This initial modelling exercise was carried out to provide simulations using the currently used model which will be a basis for comparison with updated versions of the model. The model will be adjusted during the course of this study to account for some deficiencies as discussed in Section 2. Simulations will be carried out with any new version of the model, as well as with a model (or models) obtained from elsewhere as indicated in Section 2.

The modelling exercise was also carried out to provide an indication of the magnitude of changes that might be expected during four years of acid application. Details of the model and model inputs are provided in Section 6 (to avoid repetition of procedures used). The simulation was carried out using the same acid input levels as in the artificial acidification experiment (0.3, 0.6, 1.2, 2.4, and 4.8 kmol H<sup>+</sup> ha<sup>-1</sup> yr<sup>-1</sup>). The response curves are presented in Figures 3 to 5. The results indicate that pH could drop about 0.2 units at the highest acid input level within the four year experimental period. The base saturation level is estimated to decrease from 0.53 to about 0.40 in this period, while the Al levels will show minor increases. (Note that the pH, BS and Al curves level off abruptly. This is essentially an artifact since the model equations do not adequately simulate changes when extremely low levels of bases are reached. Consequently values represented by the horizontal parts of the curves should not be compared).

The estimated current levels of atmospheric acid deposition were not accounted for in these simulations. This level is 0.22 kmol H<sup>+</sup> ha<sup>-1</sup> yr<sup>-1</sup>, and adding this amount to levels used in the simulations will result in slightly steeper slopes for each of the curves. The simulations should also account for the additional water added in irrigation of the acidification plots. However, this amount is only about 15 mm per year and is considered to be within the year-to-year variation of the total precipitation (taken to be 470 mm at this site).

Figure 3. pH changes for the Ft. McMurray plot soil.

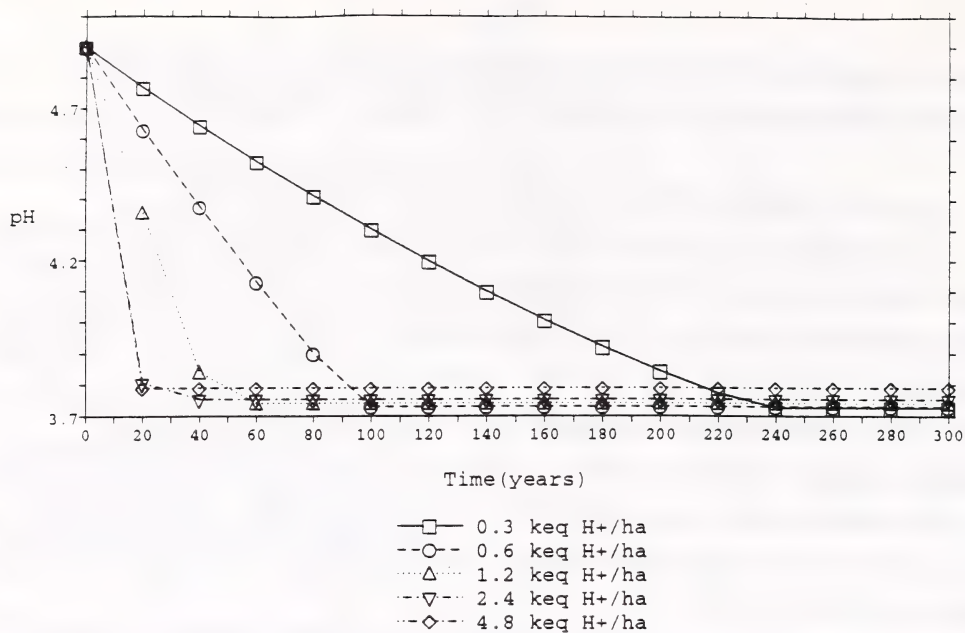


Figure 4. Base saturation (BS) changes for the Ft. McMurray plot soil.

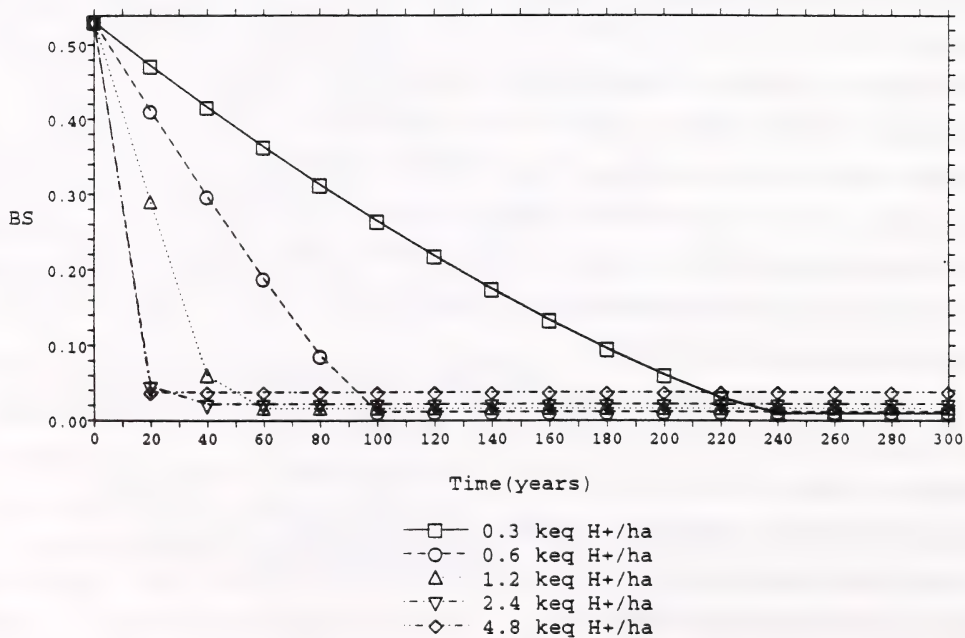
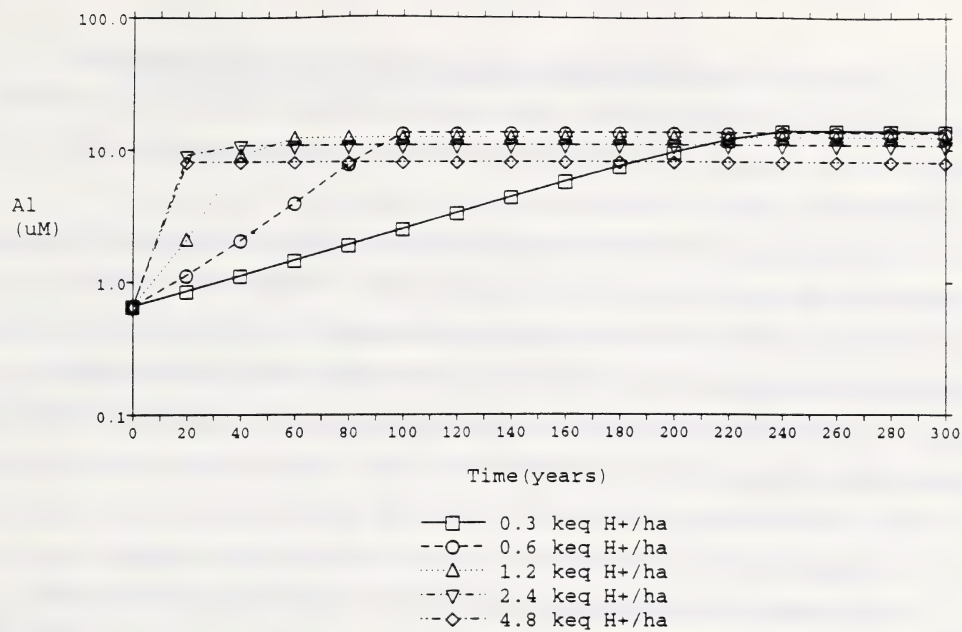


Figure 5. Soluble Al changes for the Ft. McMurray plot soil.



These results suggest that any pH changes over the period of the acidification experiment will be small and difficult to detect. Base saturation differences should be measurable and it is anticipated that the composite sampling methods and replication will enable natural variation to be accounted for.

The long term precipitation and evapotranspiration averages used in the model may differ somewhat from real values over the term of the experiments. Any differences should be examined in terms of modelling results. It is recommended that actual precipitation values be used in modelling and that evapotranspiration be estimated by the most reliable methods available using meteorological data from the site. Consequently, meteorological information should be collected at the site over the remaining three year period of the project.

#### 4.5 CONCLUSIONS

The model results showed that during the four year period of the Acid Deposition Project base saturation would be reduced by more than 10% at the highest loading rate and would be the most readily measurable of the acidification parameters. Meteorological data should be collected at the site to enable input of measured values instead of long term average data. Moreover, it would be preferable to monitor air and precipitation at the site to enable more precise values to be used in calculating effective acidity applied to soils; i.e., accurate atmospheric chemistry data are needed to add to the artificially added acid levels.

## 5. LONG TERM MONITORING SITE EVALUATION

### 5.1 INTRODUCTION

Long term soil acidification monitoring was initiated by Alberta Environment in September, 1981, to provide an early warning of the potentially adverse effects of acidic atmospheric deposition on Alberta's soil resource. The objective of the program is to detect subtle changes in soil properties indicative of potentially long-term changes in the ability of the soil to sustain plant growth. A full description of the program, explanation of the criteria for selecting sites, and results of the first eight years of monitoring have been documented by Roberts et al. (1989). The objective of the work reported herein is to assess the ability of the soils at the long term monitoring sites to behave as early warning sites. This is addressed in this initial stage of the project by applying the ARC model (Abboud and Turchenek 1990) to estimate changes in soil properties resulting from estimated current and possible future loadings of acidic substances. Upon completion of model refinement and validation, the soils will be reassessed with the updated model. Information on buffering capacities and mechanisms in these soils will be obtained through inclusion of samples from the long term sites in the work described for the inorganic soil research component introduced in Section 2 of this report.

### 5.2 MATERIALS AND METHODS

All modelling exercises in this project were carried out together using the same model and model parameters. Consequently, to avoid repetition, the modelling methodology and description of soil inputs for the long term monitoring sites are included in the 'Materials and Methods' section for the project component concerning critical load determinations in Section 6. Descriptions of soils in the long term monitoring plots can be found in Roberts et al. (1989).

### 5.3 RESULTS

Results of modelling in the form of response curves and tables of threshold values are given in Figures 21 to 44 and Table 6 in Section 6.

### 5.4 DISCUSSION

Discussion of modelling results for the long term modelling sites in terms of threshold or critical levels of soil properties is included in the discussions in Section 6. Additional comments on an individual site basis are provided in this section. The comments are made in terms of estimated



current levels of acid deposition derived during the Acid Deposition Research Program as reported by Abboud and Turchenek (1990).

#### 5.4.1 Ft. McMurray Site

Short term model results are discussed in terms of estimated ambient deposition levels of  $0.22 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  with changes indicated as follows:

pH 4.5  $\Rightarrow$  4.3                      20 yr

pH 4.5  $\Rightarrow$  4.1                      50 yr

BS .22  $\Rightarrow$  .14                      20 yr

BS .22  $\Rightarrow$  .02                      50 yr

Al 1.5  $\Rightarrow$   $2\mu\text{M}$                       20 yr

Al 1.5  $\Rightarrow$   $3.5\mu\text{M}$                       50 yr

The total base content was low such that bases were depleted very rapidly in this model scenario. This resulted in the model stopping further calculation when bases were depleted at pH 4.0 to 4.1. It is known that soils in the region can have pH levels as low as 3.5. The results for this soil are basically a model artifact at the low BS values, as discussed in Section 6.

The short term results suggest that pH differences will be difficult to detect because of the narrow range from 4.5 to 4.0. However, BS measures show a wider range and should be detectable if they in fact diminish as a consequence of external acidic additions.

#### 5.4.2 Cold Lake Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.18 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH 4.8  $\Rightarrow$  4.7                      20 yr

pH 4.8  $\Rightarrow$  4.5                      50 yr

BS .67  $\Rightarrow$  .62                      20 yr

BS .67  $\Rightarrow$  .53                      50 yr

Al 1  $\Rightarrow$  1 $\mu$ M                      20 yr

Al 1  $\Rightarrow$  2 $\mu$ M                      50 yr

The total base content was low but somewhat higher than that of the Ft. McMurray soil. pH changes will be difficult to detect in the short term because of the very narrow range from 4.8 to 4.5. BS and Al levels did not display as wide a range as in the Ft. McMurray soil. The 20 year change above may not be significant if considered in terms of natural spatial and temporal variation. If acid inputs levels increase, the changes in BS will be somewhat larger, but pH changes will still be in a relatively narrow range.

#### 5.4.3 High Prairie Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of 0.18 kmol ha<sup>-1</sup> yr<sup>-1</sup> are as follows:

pH 5.0  $\Rightarrow$  4.9                      20 yr

pH 5.0  $\Rightarrow$  4.7                      50 yr

BS .46  $\Rightarrow$  .42                      20 yr

BS .46  $\Rightarrow$  .36                      50 yr

Al .8  $\Rightarrow$  .8 $\mu$ M                      20 yr

Al .8  $\Rightarrow$  .9 $\mu$ M                      50 yr

The total base content is similar to that of the Cold lake soil, but the initial BS is lower. pH changes within 50 years would not be detectable at current acid deposition levels. BS changes may be detectable if natural variation can be accounted for. Al levels remain basically constant over the short term. At higher acid input rates, a pH change of about 0.5 units and larger BS reduction would likely be detectable.

#### 5.4.4 Bruderheim Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.84 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH 4.6  $\Rightarrow$  4.3                      20 yr

pH 4.6  $\Rightarrow$  3.9                      50 yr

BS .51  $\Rightarrow$  .38                      20 yr

BS .51  $\Rightarrow$  .18                      50 yr

Al  $2 \Rightarrow 3\mu\text{M}$                       20 yr

Al  $2 \Rightarrow 9\mu\text{M}$                       50 yr

The soil at the Bruderheim site has a higher base content but similar BS as compared to the High Prairie soil. The ambient acid deposition levels was estimated to be much higher for the Bruderheim area (Edmonton region) and changes in soil properties were consequently larger than predicted by the model for other sites. The results indicate that pH change may be noticed within 50 years, while BS should be readily detectable at 50 years and possibly at 20 years.

#### 5.4.5 Devon Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.84 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH 4.9  $\Rightarrow$  4.6                      20 yr

pH 4.9  $\Rightarrow$  4.3                      50 yr

BS .74  $\Rightarrow$  .64                      20 yr

BS .74  $\Rightarrow$  .48                      50 yr

Al .9  $\Rightarrow 1\mu\text{M}$                       20 yr

Al .9  $\Rightarrow 2\mu\text{M}$                       50 yr

The base content and base saturation of the Devon soil are higher than any of the previous soils discussed. A pH change at 20 years would likely be imperceptible, but possibly detectable at 50 years. BS levels may change noticeably in a 50 year period.

#### 5.4.6 Rocky Mountain House

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.28 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH  $4.9 \Rightarrow 4.9$                       20 yr

pH  $4.9 \Rightarrow 4.8$                       50 yr

BS  $.69 \Rightarrow .69$                       20 yr

BS  $.69 \Rightarrow .67$                       50 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       20 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       50 yr

The ambient acid deposition level predicted for this region is quite low as compared to Bruderheim and Devon sites, but similar to the other sites. Little change is predicted to occur in these soils. At high acid input levels, BS changes may be detectable.

#### 5.4.7 Twin Butte Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.84 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH  $5.7 \Rightarrow 5.6$                       20 yr

pH  $5.7 \Rightarrow 5.5$                       50 yr

BS  $.82 \Rightarrow .80$                       20 yr

BS  $.82 \Rightarrow .78$                       50 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       20 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       50 yr

The Twin Butte soil has a high exchangeable base cation content that provides it with high buffering capacity. Changes in pH, BS and Al are very small over the short term, even at the relatively high acid deposition levels for the Twin Butte area. Changes in BS may be detectable in about 100 years if the acid input levels are continued at levels near  $1 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  over that period.

#### 5.4.8 Esther Site

Short term changes according to model simulations in terms of estimated ambient deposition levels of  $0.18 \text{ kmol ha}^{-1} \text{ yr}^{-1}$  are as follows:

pH  $5.7 \Rightarrow 5.6$                       20 yr

pH  $5.7 \Rightarrow 5.5$                       50 yr

BS  $.83 \Rightarrow .81$                       20 yr

BS  $.83 \Rightarrow .77$                       50 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       20 yr

Al  $<1 \Rightarrow <1\mu\text{M}$                       50 yr

The Chernozemic soil at the Esther site is very sandy but has a relatively high base cation content that provides it with more buffering capability than the Brunisolic and Luvisolic soils. The changes in pH, BS and Al are very low at the ambient acid deposition levels. Consequently, changes in the soil would be detectable only if acid inputs were somewhat higher than assumed in the simulations.

#### 5.5 CONCLUSIONS

The soils in the long term monitoring site program span a range of buffering capabilities as based on base saturation levels. Most of the soils in the program appear to be appropriate as early warning indicators. An exception is the Twin Butte soil which is strongly buffered and would not likely show chemical changes even under very high acidic loadings. In measuring changes over time, pH in most soils will not show substantial decreases if they are in fact influenced by acidic inputs. The base saturation levels on the other hand may show significant changes and should be carefully examined during the program.



## 6. CRITICAL LOAD DETERMINATION

### 6.1 INTRODUCTION

The concept of a critical or threshold value of a soil property was used to evaluate acid deposition impacts on soils. This is defined as a quantitative value of a soil property above or below which a system would be regarded as being damaged. Different pH threshold values can be established for evaluations of acid deposition effects on soils. The evaluation was carried out by application of the ARC model (Turchenek and Abboud 1988) which simulates the soil chemical processes directly related to acidity and acidification of soils, and which predicts the associated soil properties of pH, base saturation and soluble  $Al^{3+}$  concentration. The ARC model is described in detail in Turchenek and Abboud (1988) and Abboud and Turchenek (1990). This model is adapted from the Bloom and Grigal (1986) model, the modifications being related to calculations of acid inputs and acidification processes and to the method of output of model results.

### 6.2 MATERIALS AND METHODS

#### 6.2.1 Soil Selection

Soils from the sulphate experiments (Section 2), the model validation experiment (Section 4), and from the Long Term Monitoring plots (Section 5) were analyzed in terms of threshold values with respect to current and possible future levels of acidic deposition. All soils except that from the Twin Butte site were very sandy and consequently low in base cation content and buffering capacity. The Twin Butte soil is developed on finer sediments and has a considerably higher base cation content than the other soils. The classification, pH, and other properties of the soils are presented in Table 5 which provides all the input parameters for the modelling exercises.

#### 6.2.2 Soil Data Inputs

Soil pH values were obtained by the  $CaCl_2$  method. Cation exchange capacity and exchangeable bases in soils were obtained by the ammonium acetate extraction method (McKeague et al. 1978).

Little data for partial pressure of  $CO_2$  in the soil atmosphere is available, and since  $P_{CO_2}$  is quite variable, the value of 0.005 atmosphere was used in this project.

Table 5. Input data for soil acidification simulations using the ARC model.

Location	Ft. McMurray1	Peers	Edson	Hinton1	Hinton2	Ft. McMurray2	Cold Lake
Soil Subgroup	Eluviated Dystic Brunisol	Eluviated Dystic Brunisol	Eluviated Dystic Brunisol	Orthic Humo-Ferrie Podzol	Orthic Humo-Ferrie Podzol	Eluviated Dystic Brunisol	Eluviated Dystic Brunisol
Soil Series	Mildred	Peers <sup>ac</sup>	Peers <sup>ac</sup>	Hornbeck	Hornbeck <sup>ac</sup>	Mildred	Liza
Annual Precipitation (cm)	52	55	55	60	60	47	47
Annual Evapotranspiration (cm)	30	38	38	38	38	30	35
Years of Iteration	300	300	300	300	300	300	300
Increment of Years	20	20	20	20	20	20	20
Soil pH (CaCl <sub>2</sub> )	4.9	4.8	3.8	4.0	4.4	4.5	4.8
Total Soil Bases (kmol(+)/ha <sup>-1</sup> )	51	168	150	118	35	11	38
Soil CEC (kmol(+)/ha <sup>-1</sup> )	96	310	348	303	138	51	57
Base Saturation (%)	53	54	43	39	25	22	67
CO <sub>2</sub> Partial Pressure (atm)	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Activity Coefficient of Al <sup>3+</sup>	0.82	0.82	0.82	0.82	0.82	0.82	0.82
Activity Coefficient of Al <sup>2+</sup>	0.92	0.92	0.92	0.92	0.92	0.92	0.92
a in pH = a(BS) + b	2.25	2.25	2.25	2.25	2.25	2.25	2.25
b in pH = a(BS) + b	3.52	3.52	3.52	3.52	3.52	3.52	3.52
Total H <sup>+</sup> Input (kmol ha <sup>-1</sup> yr <sup>-1</sup> )	0.22, 0.86	0.28, 0.47	0.28, 0.47	0.28, 0.47	0.28, 0.47	0.22, 0.86	0.18, 0.33
Total Equiv S Input (kg ha <sup>-1</sup> yr <sup>-1</sup> )	3.5, 13.8	4.5, 7.5	4.5, 7.5	4.5, 7.5	4.5, 7.5	3.5, 13.8	2.9, 5.3
Total Equiv SO <sub>2</sub> Input (kg ha <sup>-1</sup> yr <sup>-1</sup> )	7.0, 27.6	9.0, 15.0	9.0, 15.0	9.0, 15.0	9.0, 15.0	7.0, 27.6	5.8, 10.6

..... Continued

<sup>ac</sup> - acidic variant of Peers which is an Eluviated Eutric Brunisol.

<sup>ac</sup> - variant of Hornbeck having clay subsoil within 1 m.

Table 3. Concluded.

Location	High Prairie	Bruderheim	Devon	Rocky Mountain House	Twin Butte	Esther
Soil Subgroup	Eluviated Dystic Brunisol	Eluviated Dystic Brunisol	Eluviated Dystic Brunisol	Brunisolic Gray Luvisol	Orthic Black	Orthic Dark Brown
Soil Series	Heart	Nestow	Nestow	Prentice	Dunvargan	Wainright
Annual Precipitation (cm)	50	47	47	56	54	35
Annual Evapotranspiration (cm)	38	42	42	38	41	40
Years of Iteration	300	300	300	300	300	300
Increment of Years	20	20	20	20	20	20
Soil pH (CaCl <sub>2</sub> )	5.0	4.6	4.9	4.9	5.7	5.7
Total Soil Bases (kmol(+)ha <sup>-1</sup> )	37	66	119	217	670	193
Soil CEC (kmol(+)ha <sup>-1</sup> )	81	129	160	316	816	233
Base Saturation (%)	46	51	74	69	82	83
CO <sub>2</sub> Partial Pressure (atm)	0.005	0.005	0.005	0.005	0.005	0.005
Activity Coefficient of Al <sup>3+</sup>	0.82	0.82	0.82	0.82	0.82	0.82
Activity Coefficient of Al <sup>3+</sup>	0.92	0.92	0.92	0.92	0.92	0.92
a in pH = a(BS) + b	2.25	2.25	2.25	2.32	3.18	3.18
b in pH = a(BS) + b	3.52	3.52	3.52	3.35	3.14	3.14
Total H <sup>+</sup> Input (kmol ha <sup>-1</sup> yr <sup>-1</sup> )	0.18, 0.33	0.84, 1.14*	0.84, 1.14*	0.28, 0.47	0.84, 1.14	0.28, 0.47*
Total Equiv S Input (kg ha <sup>-1</sup> yr <sup>-1</sup> )	2.9, 5.3	7.7, 18.2	7.7, 18.2	4.5, 7.5	7.7, 18.2	4.5, 7.5
Total Equiv SO <sub>2</sub> Input (kg ha <sup>-1</sup> yr <sup>-1</sup> )	5.8, 10.6	15.4, 36.5*	15.4, 36.5*	9.0, 15.0	15.4, 36.5	9.0, 15.0

\* - using data for ADRP Region 9 (Calgary area), assuming that deposition near urban centre of Edmonton is similar.

Activity coefficients of  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})^{2+}$  were 0.82 and 0.92, respectively, as suggested by Bloom and Grigal (1985).

The input data for soil pH, CEC, and sum of bases were weighted mean values for the top 30 cm of air-dried mineral soil. Litter layers, or L, F, and H horizons, were excluded from the calculations. The thickness of the soil horizons and the bulk density were considered in computing the means. The calculations were made as previously documented by Turchenek and Abboud (1988) and Abboud and Turchenek (1990).

#### 6.2.3 Acid Deposition Data

Values for total effective acidity were those determined in the Alberta Government/Industry Acid Deposition Research Program (ADRP) as reported by Abboud and Turchenek (1990). In this study, the province was divided into 10 emission regions and the deposition values were estimated for each of these. The chemistry of wet deposition in the Calgary region was based on monitoring results from the Crossfield air quality monitoring stations established by the ADRP. Data for the other regions were derived from CANSAP and Alberta Environment precipitation chemistry stations. The wet chemistry data required for soil simulations are pH, and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations. For all regions, the data used were mean values for two years, from mid-1985 to mid-1987.

Dry deposition inputs were added to precipitation inputs to derive the total acid deposition. Data for aerosol  $\text{SO}_4^{2-}$  and  $\text{SO}_2$ , estimated in the ADRP study, were converted to equivalent acidity by assuming that each  $\text{SO}_4^{2-}$  and  $\text{SO}_2$  was associated with or would generate two  $\text{H}^+$  ions. Two deposition scenarios were derived, one a mean value representing the estimated current deposition rates, and the other a maximum value considered as a possible future level. The calculations for effective acidity are documented in more detail in Abboud and Turchenek (1990).

#### 6.2.4 Climate Data

Annual precipitation data for centres nearest to the soil sample sites were obtained from records of the Atmospheric Environment Service (1980). For annual evapotranspiration, values for average areal evapotranspiration determined by Bothe and Ames (1984) were used.



#### 6.2.5 Time

The model can be executed for any specified length of time, and simulation results can be reported for any specified increment of time within the total simulation period. Predictive soil effects data are of greatest interest in terms of the immediate and near future; i.e., the period during which pollutant emissions can be forecast. It is also of interest, from a soil development point of view, to determine soil responses to acid deposition over very long periods of time since changes in soils occur slowly. Three hundred years was arbitrarily selected for the simulation period. This time frame would not obscure the data for interpretation of short-term effects, yet would provide a longer term view of soil changes.

Twenty years was selected as the increment of time between reported values in the simulations. The main criterion for this entailed assurance that sufficient data points were obtained for plotting pH, base saturation and  $Al^{3+}$  levels over time.

#### 6.2.6 Effect of Weathering

The model can be applied either with or without weathering. If the rate of weathering is known at any pH, the rate at another pH can be calculated from the equation,

$$r = r_0 10^{-0.5(pH - pH_0)}$$

where  $r_0$  and  $pH_0$  are the initial conditions. Bloom and Grigal (1985) used the value of 0.07  $kmol(+)ha^{-1}yr^{-1}$  at a  $pH_0$  of 5.0. This was based on calculations from weathering experiments using lysimeters in Minnesota and Wisconsin. The same value was used for simulations in this project, although it is not yet known if it is appropriate for the soils from the areas sampled.

#### 6.2.7 Summary of Data Inputs

The starting parameters for soils used in simulations are given in Table 5. The taxonomy and some general descriptive features of the soils are indicated along with input data described previously. The total acid input, calculated from wetfall and dryfall acidity is also provided in Table 5 in terms of  $H^+$  input and in terms of S and  $SO_2$  equivalent inputs.



#### 6.2.8 Computations

The loss of bases is calculated on an annual basis from,

$$S = I - A - C - W$$

where S is the sum of bases lost, I is the effective acidity in the precipitation plus dryfall, A is the acid leached out of the top 25 cm of soil, C is the decrease in bicarbonate weathering due to the decrease in soil solution pH, and W is the base contribution due to weathering. At the end of each year of simulation, a new sum of bases is calculated from the sum for the previous year. New values for pH and  $Al^{3+}$  content are also calculated from equations relating pH with base saturation and pH with solution  $Al^{3+}$  concentration. A linear function describes the relationship between pH and base saturation percentage of the soil. The functions have been determined previously and reported by Abboud and Turchenek (1990).

#### 6.2.9 Model Execution and Data Outputs

The simulations were run on a Digital VAX 3100 mini-computer. Computations were made for changes in soil properties on an annual basis, but data were reported for 20-year intervals as indicated previously. Output data for each time interval included: (1) year; (2) pH of soil; (3) acid input; (4) acid output; (5) protonation; (6) change in pH; (7) base saturation; (8) sum of bases; (9) bases lost; and (10)  $Al^{3+}$ . The output of major interest consists of the changed values of soil pH, base saturation, and  $Al^{3+}$ . The ARC model was run and plots of pH, BS, and  $Al^{3+}$  versus time were generated using the data management, graphics and statistics package RS1 (BBN).

### 6.3 RESULTS AND DISCUSSION

#### 6.3.1 Soil Responses to Acid Loadings

Results of the computer simulations of acid deposition effects on the soils are shown in Figures 6 to 44. (The figures are inserted at the end of this section so as not to interrupt the text). The figures show changes in pH, base saturation, and solution  $Al^{3+}$  concentration over the 300-year time period of the simulations for mean and high inputs of acidity.

6.3.1.1 Long Term Monitoring Plot Soils. The soil from the Ft. McMurray site was the most sensitive of the Long Term Monitoring Program soils, having dropped by 0.5 pH units in 20 years at the higher loading for the region ( $0.86 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$ ). The Bruderheim soil required 45 years to drop by 0.6 pH units at a similar acid loading (although this loading was the lower one for this region). All of the sandy Brunisolic, Podzolic and Luvisolic soils decreased in pH at more rapid rates than the Chernozemic soils, including the sandy Esther soil. Those soils in which pH dropped rapidly also reached very low base saturation levels and relatively high solution Al levels.

6.3.1.2 Other Soils. The first group of soils in Table 5 were collected for studies on sulphate sorption and other properties pertaining to model inputs (Section 2). As with the Long Term Monitoring Site soils, the sandy Ft. McMurray 1 soil appeared to have the highest sensitivity to acid loadings. Its initial pH was somewhat higher than that of the Ft. McMurray 2 soil, but it dropped over 1 pH unit within 45 years. The Peers soil had the highest base cation content and was the most resistant to change in pH, as well as base saturation and Al levels. The Edson and Hinton 1 soils had very low initial pH values which were already at the presumed threshold values for soils.

6.3.1.3 General Discussion. Predictions for changes in pH, base saturation, and solution  $\text{Al}^{3+}$  levels in Alberta soils using the ARC simulation model have previously been reported by Turchenek et al. (1987, 1988). In these studies it was concluded that sandy soils with low cation exchange capacity (CEC) are the most susceptible to acid inputs, and that adverse effects would occur soonest in those soils which already have relatively low pH and base saturation levels. Soil effects simulations carried out in this project agree with the findings of the previous reports. Changes in soil properties were greatest in coarse-textured soils having low CEC and exchangeable base contents. Significant reductions in pH and base saturation occurred in coarse-textured soils within 100 years in the simulations. Increase of solution  $\text{Al}^{3+}$  concentrations to potentially toxic levels occurred in the Brunisols and Podzols with initially low pH values. The cation exchange capacities and exchangeable base cation levels in coarse-textured Chernozemic soils are most likely a consequence of their higher organic matter contents.

The model predictions are probably overestimations of actual conditions; that is, the calculated soil responses were of greater magnitude than likely could occur because of some of the assumptions made. Two of the assumptions are that exchange of  $\text{H}^+$  for base cations is complete and

that no counteracting forces are present. The counteracting forces which were not considered are neutralization by nutrient cycling and buffering by organic matter in litter layers.

### 6.3.2 Soil Responses in Relation to Threshold Values

The number of years required to reduce soil pH to threshold levels was estimated for each soil from the simulation results. The results were tabulated for responses at both mean and maximum levels of acid inputs and are presented in Table 6.

The concept of a critical or threshold value of a soil property has been used in evaluations of acid deposition impacts on soils. A critical or threshold value can be defined as a quantitative value of a soil property above or below which a system would be regarded as being damaged. Damage is not considered in terms of the soil itself, but generally in terms of the life it supports or influences. The concept enables evaluations of soil responses in terms of a standard as opposed to making comparisons based on relative differences. There is some difficulty, however, in determining threshold values because of different requirements and tolerances among organisms in relation to soil properties.

Nilsson (1986) discussed the maximum loadings of acidic and acid forming substances that soils could be exposed to. He suggested that the loadings should be no higher than those at which weathering would totally offset acid inputs such that pH and base saturation percentage of the soil would not be affected. Thus, a threshold value other than the current value of pH and base saturation was not considered to be permissible.

Posch et al. (1985) have described the concept of 'critical pH' in evaluations of acid deposition effects in Europe by the International Institute for Applied Systems Analysis (IIASA). Critical pH refers to an increased risk for forest damage due to changes in soil chemistry. The value of 4.2 was suggested for the critical  $\text{pH}(\text{H}_2\text{O})$  because buffering changes from the cation exchange range to the aluminum range at this pH (Ulrich 1981, 1983). Damage to vegetation could occur at this pH due to increased dissolved  $\text{Al}^{3+}$  concentrations in the soil solution. Aluminum toxicity depends on many factors, however, and there is no certainty as to whether there is no risk above the critical pH, nor that damage will definitely occur below it. Some criteria for relating the risk of forest damage by soil acidity to some chemical characteristics of soils have been prepared by Ulrich et al. (1984) and are presented in Table 7. These criteria were used by IIASA for evaluation of risks based on predicted emission and effects scenarios simulated by the Regional Acidification Information and Simulation (RAINS) model.

Table 6. Model predictions of time required for soils to reach threshold pH levels at estimated current and future loadings of acid deposition.

Soil Site	Acid Loading kmol(H <sup>+</sup> )ha <sup>-1</sup> yr <sup>-1</sup>	Initial pH	Threshold pH	
			5.0	4.0
Ft. McMurray	10.22	4.9	-	245
	0.86	4.9	-	45
Peers	0.28	4.8	-	>300
	0.47	4.8	-	260
Edson	0.28	3.8	-	-
	0.47	3.8	-	-
Hinton 1	0.28	4.0	-	-
	0.47	4.0	-	-
Hinton 2	0.28	4.4	-	110
	0.47	4.4	-	60
Ft. McMurray 2	0.22	4.5	-	70
	0.86	4.5	-	20
High Prairie	0.18	5.0	-	280
	0.33	5.0	-	140
Cold Lake	0.18	4.8	-	140
	0.33	4.8	-	70
Bruderheim	0.84	4.6	-	45
	1.14	4.6	-	30
Devon	0.84	4.9	-	80
	1.14	4.9	-	60
Rocky Mountain House	0.28	4.9	-	>300
	0.47	4.9	-	300
Twin Butte	0.84	5.7	270	>300
	1.14	5.7	190	300
Esther	0.27	5.7	180	>300
	0.47	5.7	110	260



Table 7. Criteria for relating risk of forest damage to some chemical characteristics of soils.<sup>1</sup>

Soil Property	Increasing Risk	High Risk	Very High Risk
pH(H <sub>2</sub> O)	≥4.2	4.0 to 4.2	<4.0
Base Saturation (%)	≥0.05	<0.05	0.0
Al <sup>3+</sup> (mmol L <sup>-1</sup> )	<25	25 to 40	>40
Ca/Al Ratio	>0.4	0.1 to 0.4	<0.1

<sup>1</sup>Source: Ulrich et al. (1984).

Levine and Ciolkosz (1988) applied a simulation model to determine the sensitivity of Pennsylvania soils to acid deposition. Soils were classified into various sensitivity classes based on the amount of time required for the soil to reach any of the following threshold values: pH(CaCl<sub>2</sub>) of 4.0 or less in both A and B horizons, or soil solution Al<sup>3+</sup> concentration of 1.0 mg L<sup>-1</sup> in the A horizon, or 0.1 mg L<sup>-1</sup> in the B horizon. This pH value was chosen because of the high acidity and associated conditions such as low base saturation and microbial activity, high rates of mineral weathering and leaching of heavy metals, and presence of significant levels of exchangeable H<sup>+</sup> and Al<sup>3+</sup>. The level of 1.0 mg L<sup>-1</sup> Al<sup>3+</sup> in the A horizon was chosen to represent a level toxic to some plant species and the 0.1 mg L<sup>-1</sup> level in the B horizon was chosen to represent a level toxic to brook trout. This latter level was selected under the assumption that soil water would move to groundwater and water bodies with little additional change.

Sensitivity classes consisted of the following: (1) very sensitive soils, or those that reach a threshold value between 0 and 30 years; (2) sensitive soils, or those which reach a threshold value between 30 and 60 years; (3) slightly sensitive soils, or those that reach a threshold value between 60 and 90 years; and (4) nonsensitive soils, or those that don't reach a threshold value in 90 years. The 30-year increments were chosen to represent the length of an average human generation.

Simulation results were presented in terms of two different threshold values of soil pH in Table 6. The foregoing explains the reasons for selection of these particular threshold values.

The highest value (i.e., 5.0) was selected as a pH level below which soil conditions adverse to crop production would occur. The pH calculated in the soil acidification model is that which would be obtained by measurement of a soil sample in CaCl<sub>2</sub> solution. The equivalent pH determined in water is 0.5 to 0.8 units higher. Discussions of plant growth in relation to soil acidity



are generally in terms of pH determined in water. Soils in the range of pH(H<sub>2</sub>O) 5.6-6.0 are sufficiently acidic to cause serious loss in yields of most crops in Alberta (Penney et al. 1977; Hoyt et al. 1981). The lower limit of this range, equal to pH (CaCl<sub>2</sub>) of about 5.0, was considered by Abboud and Turchenek (1990) as the threshold value for crop growth. Loss of crop productivity in acidic soils is due to reduced availability of some plant nutrients, metal element toxicities, and restriction of nitrification and nitrogen fixation by microorganisms (Hoyt et al. 1981). Rhizobia in particular are sensitive to soil pH (H<sub>2</sub>O) below about 6.0 (Visser et al. 1987).

The second threshold level, pH(CaCl<sub>2</sub>) 4.0, was selected solely on the basis of prior use by Levine and Ciolkosz (1988). The reasons for use of this value were indicated previously in this section. From the above discussion on agricultural soils, however, it is apparent that this pH cannot be applied in relation to crop growth and that it is relevant only to evaluations of forested soils.

A low threshold value in the area of pH(CaCl<sub>2</sub>) of 3.5 may also be pertinent to Alberta soils. Many forested soils in Alberta already have surface soil pH values of about 4.0 and less (Turchenek 1982; Abboud and Turchenek 1990). Low pH values were likewise found in some soils in this study (Edson and Hinton sites, Table 5). The forest communities apparently function well in these low pH soils. This suggests a critical (threshold) pH of 4.0 may be high, and the pH(H<sub>2</sub>O) 4.2 level suggested by Ulrich et al. (1984) may be more appropriate. This pH value is equivalent to about pH 3.4 to 3.7 for determinations in 0.01 M CaCl<sub>2</sub>.

It is desirable to provide evaluations on properties other than, or in addition to, soil pH. Soil pH varies both spatially and temporally, and measurement and monitoring in relation to loadings are difficult. Therefore, use of multiple criteria such as those of Ulrich et al. (1984) and Levine and Ciolkosz (1988) is preferred. Nevertheless, only threshold values for pH were considered in this project for reasons outlined below.

The two other properties simulated by the acidification model are base saturation and solution Al<sup>3+</sup> content. Aluminum levels are calculated directly from pH values. Thus, each of the threshold pH values is accompanied by a specific Al<sup>3+</sup> level as follows: 0.5 mM at pH 5.0, 6 mM at pH 4.0, and 30 mM at pH 3.5. Different threshold levels for Al<sup>3+</sup> which have been suggested are 10 mM (Bloom and Grigal 1985), 25 mM (Ulrich et al. 1984), and 40 mM (Levine and Ciolkosz 1988). Plant tolerances to Al<sup>3+</sup> are highly variable and it isn't possible to consider only one threshold Al<sup>3+</sup> level with either crop or forest species (Foy 1984; Morrison 1984). It would appear, however, that at a pH of 4.0, the Al<sup>3+</sup> levels from the simulations would be sufficiently low for most species, and even at pH 3.5 the Al<sup>3+</sup> level could be tolerable. However, the dependence of solution Al<sup>3+</sup> on pH becomes

very sensitive at this pH. At pH 3.4 the  $\text{Al}^{3+}$  level is about 40 mmol, or 10 mmol higher than at pH 3.5. A  $\text{pH}(\text{CaCl}_2)$  of 4.0 for forest soils thus seems to be an appropriate threshold level, notwithstanding the fact that some soils already are more acidic than this.

The other soil property given in simulations output is base saturation percentage. Base saturation does not exactly correspond to pH as might be expected from the linear relationship between the two properties. The regression of pH on BS is based on a large number of samples with considerable scatter about the regression line. Base saturation in the model is calculated from the slope of the regression line (Abboud and Turchenek 1990). The intercept differs for each soil modelled depending on whether it originally lies above or below the line. The minimum pH attained is dependent on the intercept. Thus, pH differs at the same BS in different soils, and vice versa.

For soils in which the pH-BS relationship conforms exactly or close to the linear relationship, the BS ranges from 0.58 to 0.66 among the soil orders at pH ( $\text{CaCl}_2$ ) 5.0, from 0.21 to 0.28 at pH 4.0, and from 0.00 to 0.11 at pH 3.5. Ulrich (1984) indicated that a BS of 0.05 might be a threshold value for forest soils. Thus, the BS in Alberta soils may reach values below this at pH 3.5. It would appear that, as discussed above, pH 4.0 is a more suitable threshold value than pH 3.5, while the BS at pH 5.0 indicates a system that is still dominated by base cations.

Some model results showed that base saturation diminished to levels near zero while pH values were still well above 3.5 (e.g., Hinton 2 site). These are not considered to be probable responses but are rather a consequence of weakness in the model at very low pH and base saturation levels. Such results indicate the need to further develop the model to accommodate these soil conditions which seem to occur commonly in forested sandy soils in Alberta.

A critical load of  $0.3 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$  was suggested for a soil of the Mildred series near Ft. McMurray by Turchenek and Abboud (1988) and Singleton et al. (1988). This value was based on a potential pH decrease to about 3.5 within 100 to 150 years if the acidic deposition level were maintained at  $0.4 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$  or higher, but would not attain this if the deposition were  $0.2 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$  or less. In the current study, the Mildred 2 soil at Ft. McMurray also appeared to be the most sensitive. A deposition level would result in a pH decrease of about 0.5 units along with a large drop in base saturation. It was noted in Section 5 that the BS would decrease to near zero within 50 years at an acid deposition level of  $0.22 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$ . The BS would thus be below the critical level of 0.05 suggested by Ulrich et al. (1984, Table 6). Aluminum levels did not increase above the threshold value of 2  $\mu\text{M}$  suggested by Ulrich et al. (1984). The depression of BS to  $<0.05$  in the Ft. McMurray 2 soil suggests that the critical load may be less than  $0.3 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$  as

previously suggested and may be about  $0.2 \text{ kmol}(\text{H}^+)\text{ha}^{-1}\text{yr}^{-1}$ . Note however that there is considerable uncertainty in these figures due in part to insufficient information about these soils and to modelling inadequacies as noted in the following section.

## 6.4 CONCLUSIONS

The results of simulations using the ARC model were in agreement with results of previous studies in which coarse-textured soils within various soil orders were found to be the most readily affected by acidic inputs. It is predicted that changes due to acid stress will be greatest in sandy soils of the Dystric Brunisol and the Orthic Humo-Ferric Podzol taxonomic groups. Significant reductions in pH and base saturation occurred in these soils within 100 years in the simulations. The model results show that some of these soils may be acidified even at the current acid loading rates. Increases in solution  $\text{Al}^{3+}$  to potentially toxic concentrations were also indicated by the simulations of these soils.

The two Chernozemic soils examined in this study were well buffered. The coarse-textured Esther soil had relatively high cation exchange capacities and exchangeable base cation levels as a consequence of relatively high organic matter content in the surface horizon.

In interpreting the modelling results, it is stressed that not all acid neutralizing factors were taken into consideration (e.g., nutrient cycling) in the acidification simulations and, therefore, the responses found are more severe than may actually occur in ecosystems. Natural soil variability must also be considered in analyzing the results. Changes in pH, for example, may fall within the temporal and spatial variability of acidity in soils. It is especially important that further modelling efforts include buffering due to organic matter in the litter layers of forest soils.

The performance of the model at low pH and base saturation values indicates the need for adjustments to the model. The model was designed to simulate soil buffering due to cation exchange. Aluminum buffering becomes significant below about pH 5, and the model, therefore, may require an alternative mechanism to account for this buffering mechanism.

There is uncertainty in establishing critical loads for the forest soils examined in this study. The pH, BS and Al levels in some cases needs to be examined closely. An example is the very low BS occurring above pH 4 in the Ft. McMurray 2 soil. From a critical loading point of view, information about actual solution Al levels in low pH soils is needed. The model shows that some very low pH soils could have Al approaching levels toxic to plants. Actual Al levels should be examined in forest soils in relation to establishing critical loads.



In summary, recommendations are as follows:

- 1) The currently used model needs to be further developed to account for processes in Alberta soils more realistically.
- 2) Measurements of Al levels in low pH forest soils should be obtained along with determinations of Al-BS-pH relationships.

These recommendations have been made in previous studies and are incorporated in the 4 year ADP soil research program. The information obtained will enable evaluation of threshold or critical levels of Al, BS and pH more thoroughly with respect to soils and vegetation of ecosystems in Alberta.

Figure 6. pH changes for the Ft. McMurray site 1 soil.

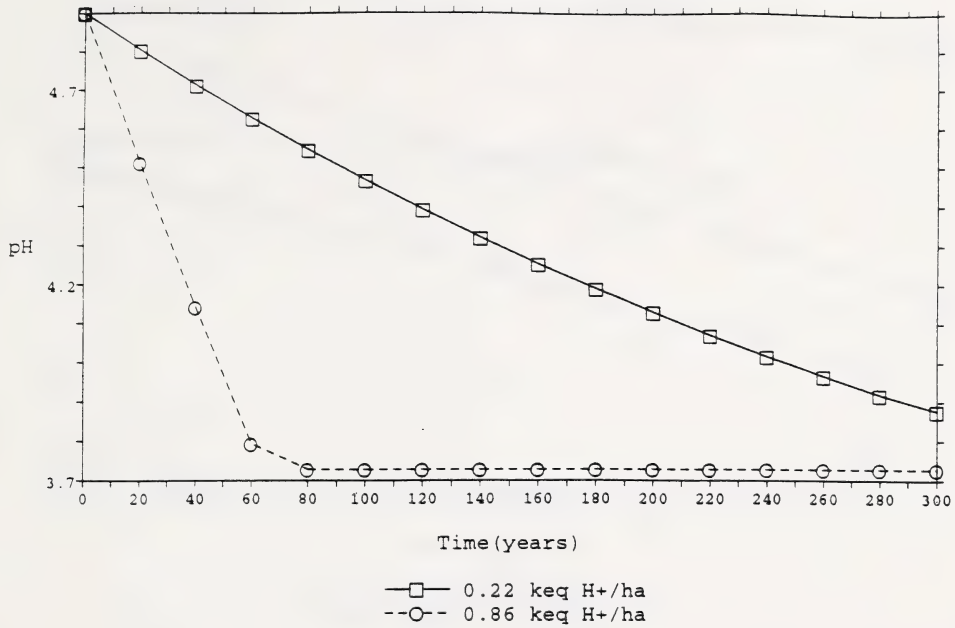


Figure 7. Base saturation (BS) changes for the Ft. McMurray site 1 soil.

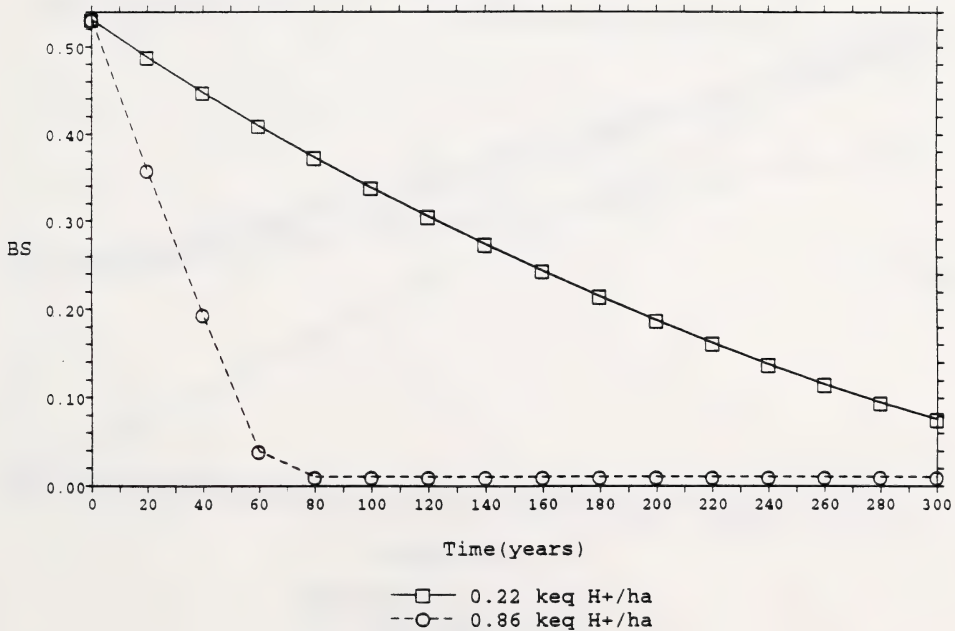




Figure 8. Soluble Al changes for the Ft. McMurray site 1 soil.

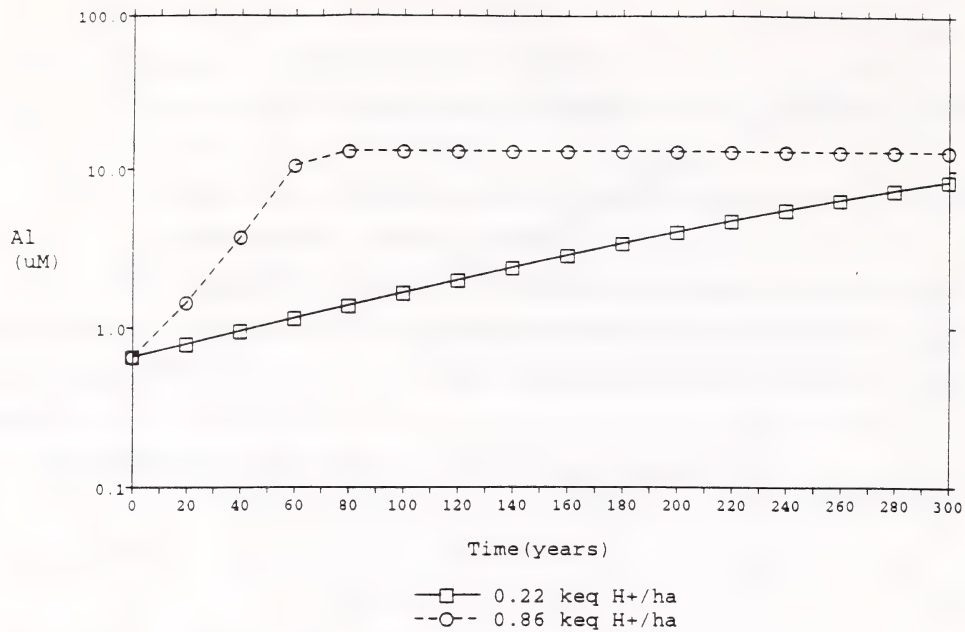


Figure 9. pH changes for the Peers site soil.

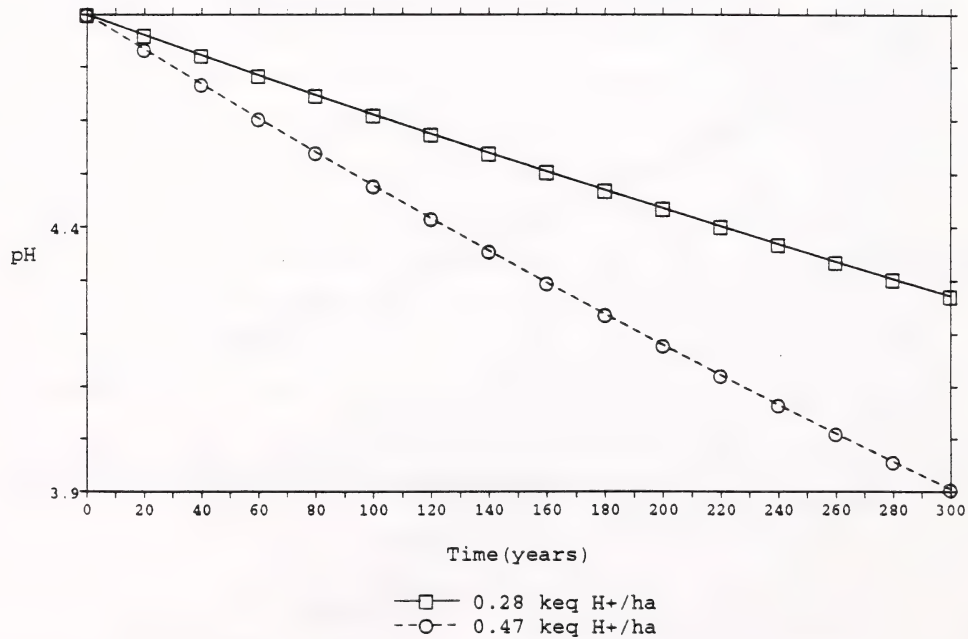


Figure 10. Base saturation (BS) changes for the Peers site soil.

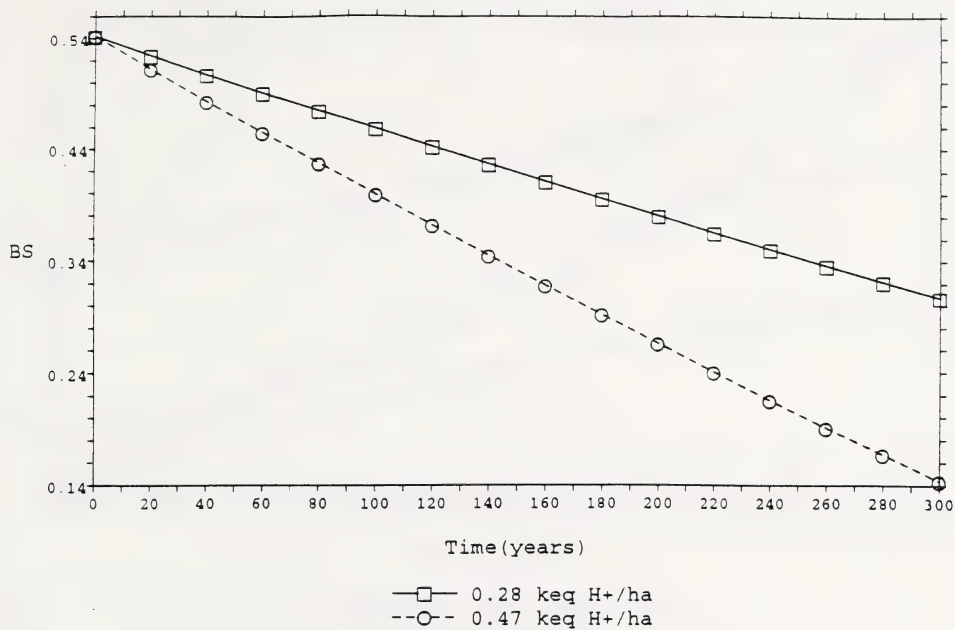


Figure 11. Soluble Al changes for the Peers site soil.

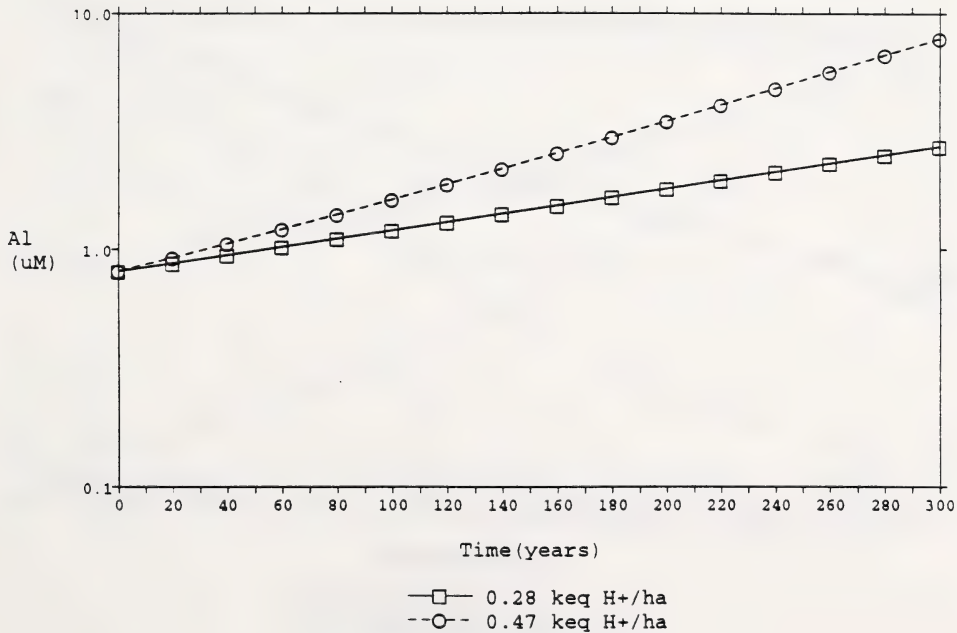


Figure 12. pH changes for the Edson site soil.

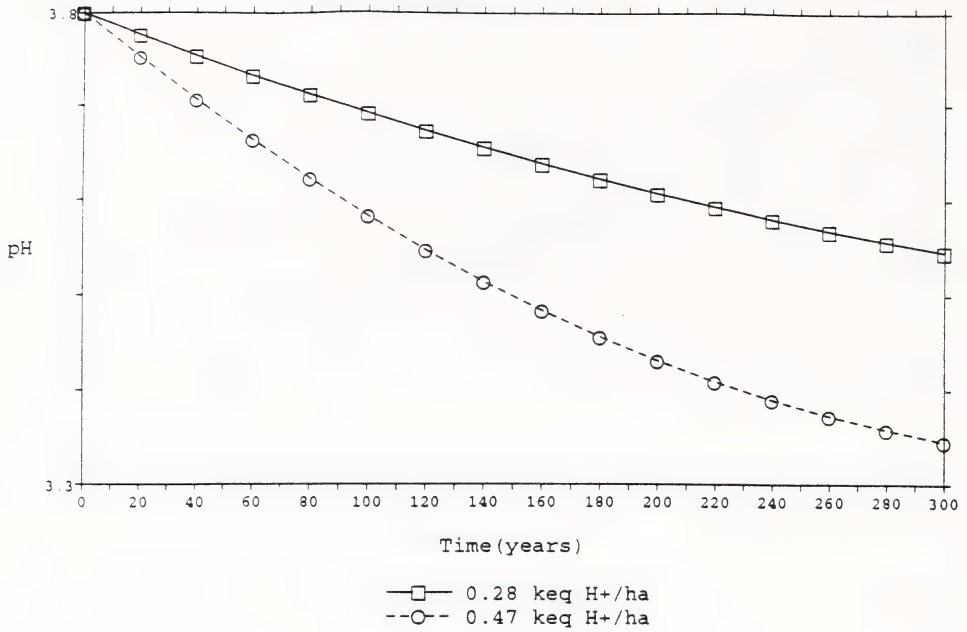


Figure 13. Base saturation (BS) changes for the Edson site soil.

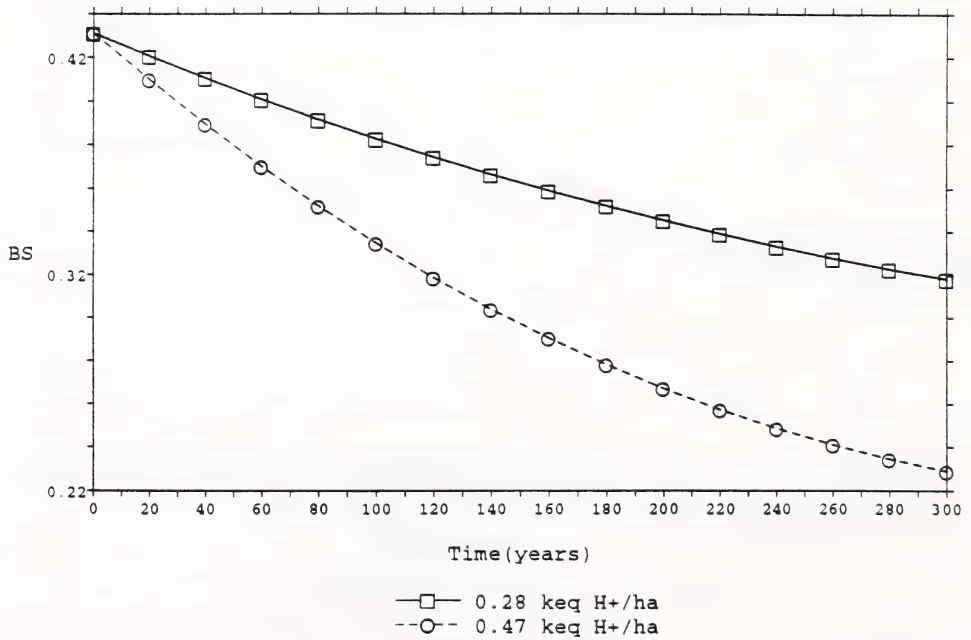


Figure 14. Soluble Al changes for the Edson site soil.

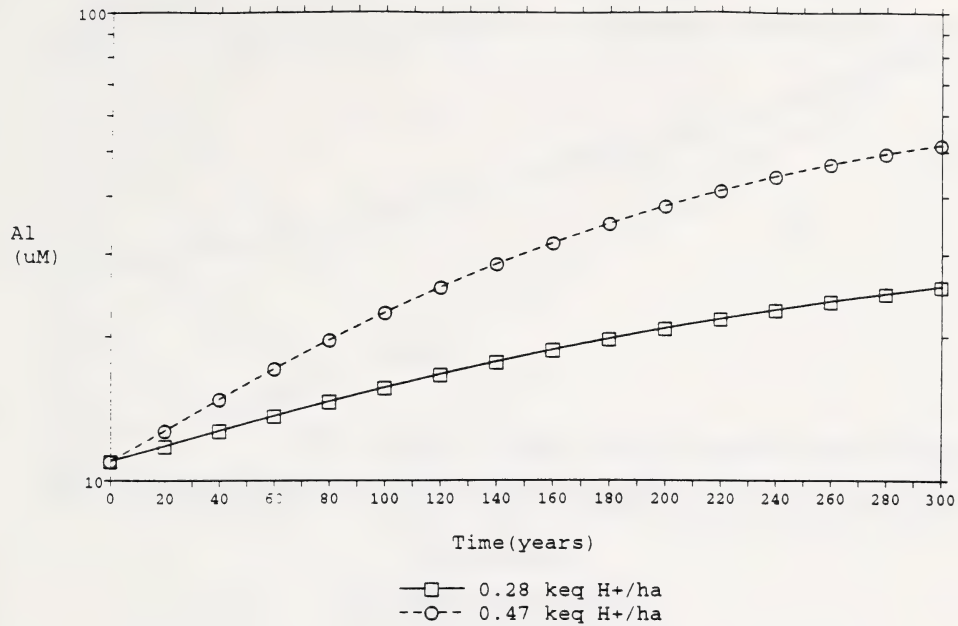


Figure 15. pH changes for the Hinton1 site soil.

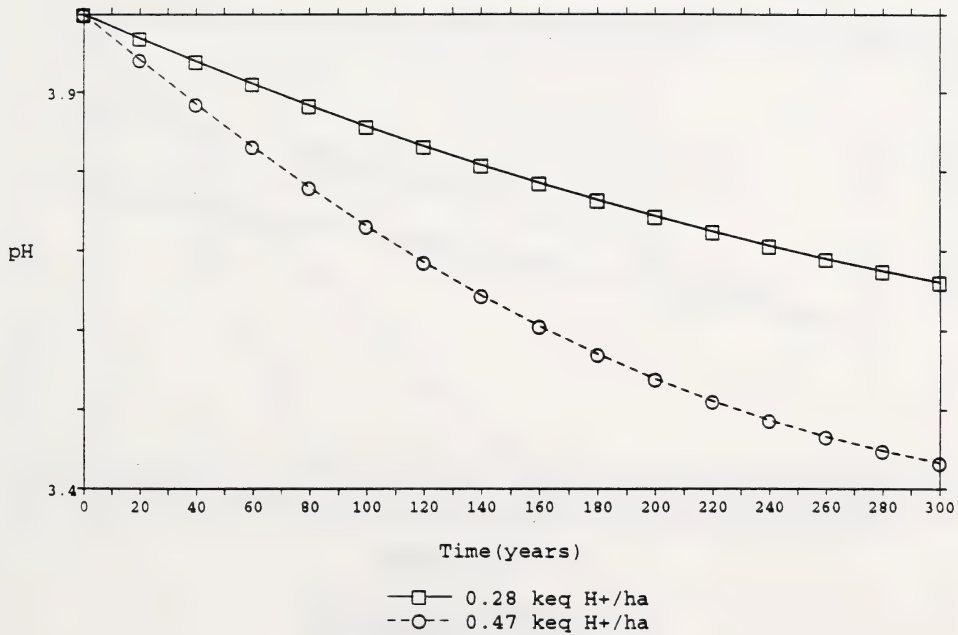


Figure 16. Base saturation (BS) changes for the Hinton1 site soil.

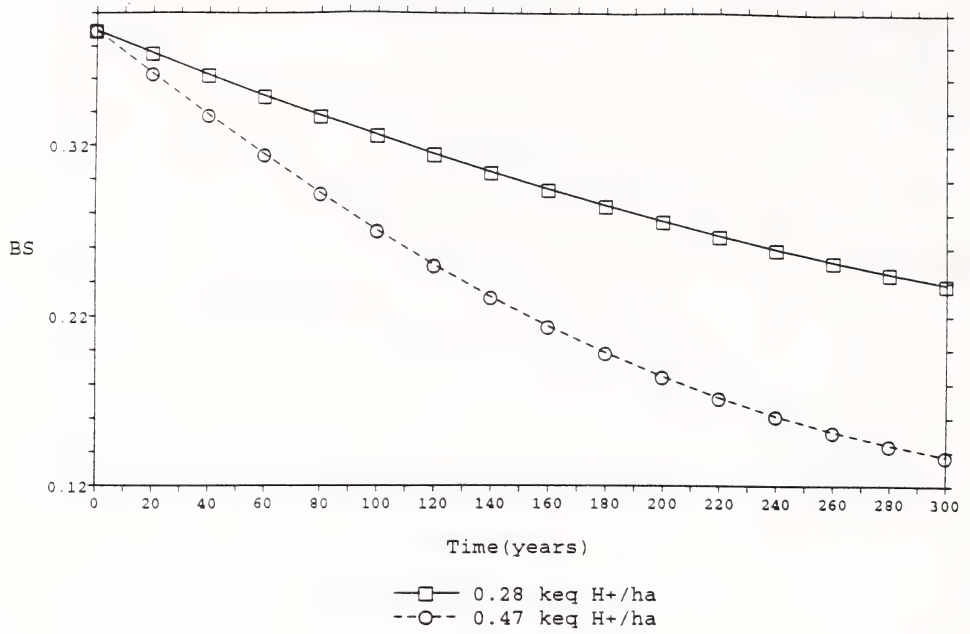


Figure 17. Soluble Al changes for the Hinton1 site soil.

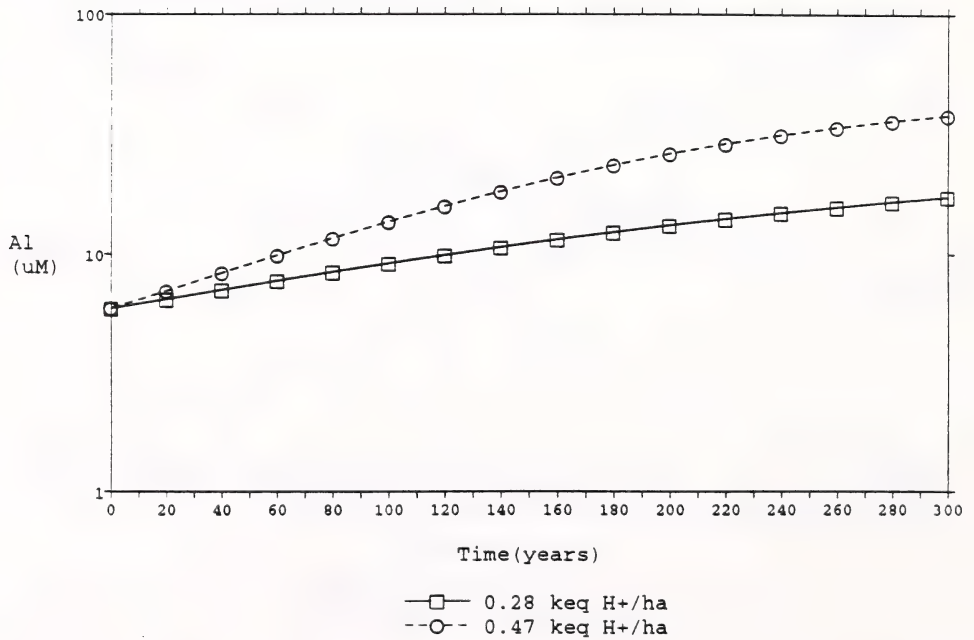




Figure 18. pH changes for the Hinton2 site soil.

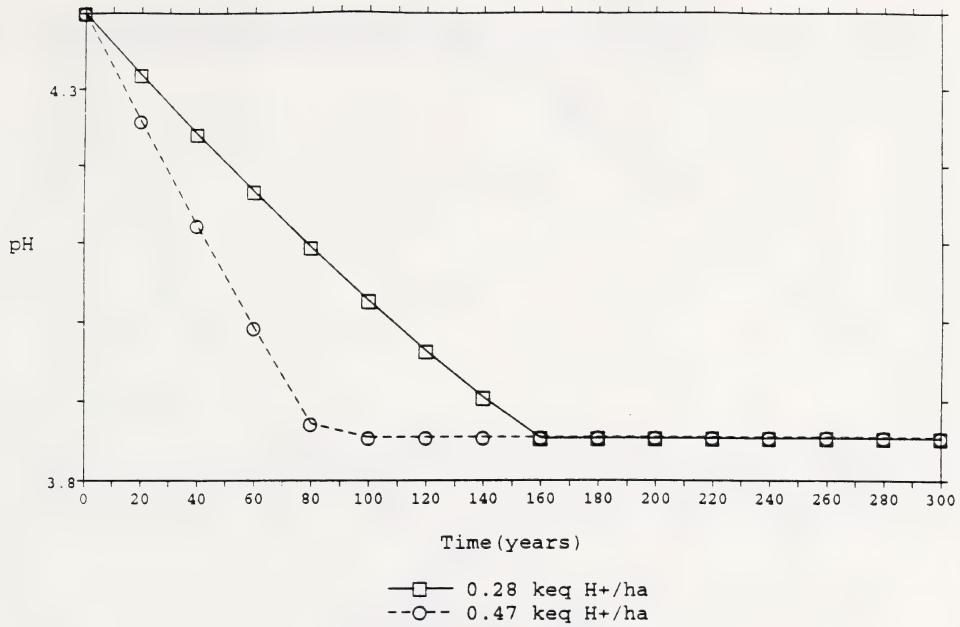


Figure 19. Base saturation (BS) changes for the Hinton2 site soil.

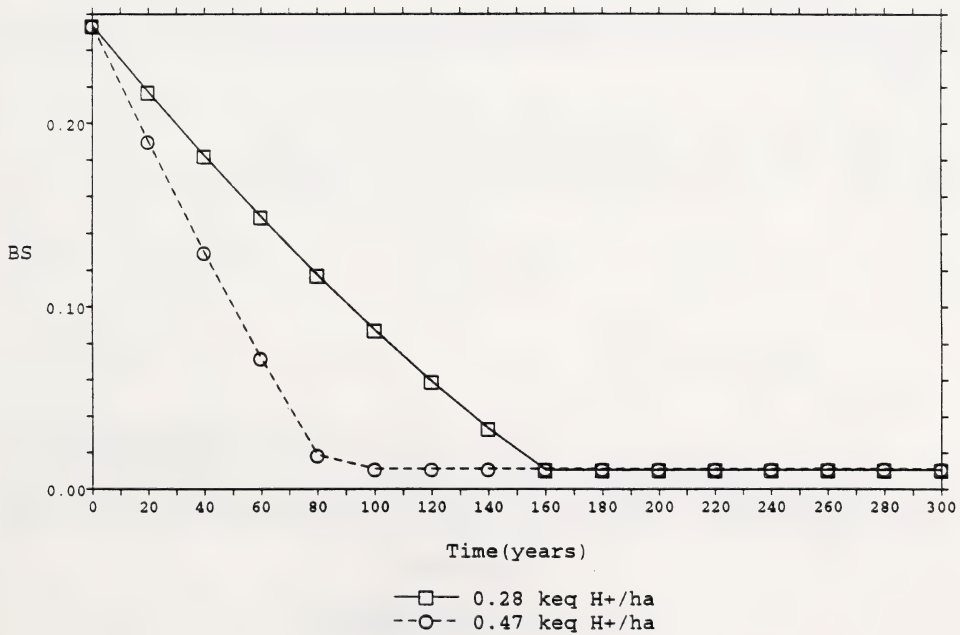


Figure 20. Soluble Al changes for the Hinton2 site soil.

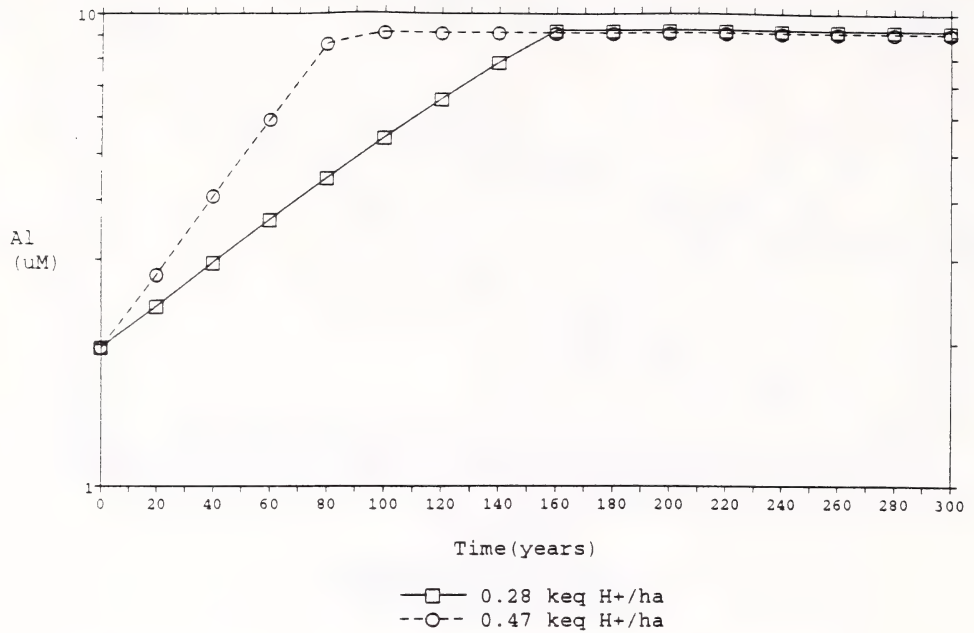


Figure 21. pH changes for the Ft. McMurray site 2 soil.

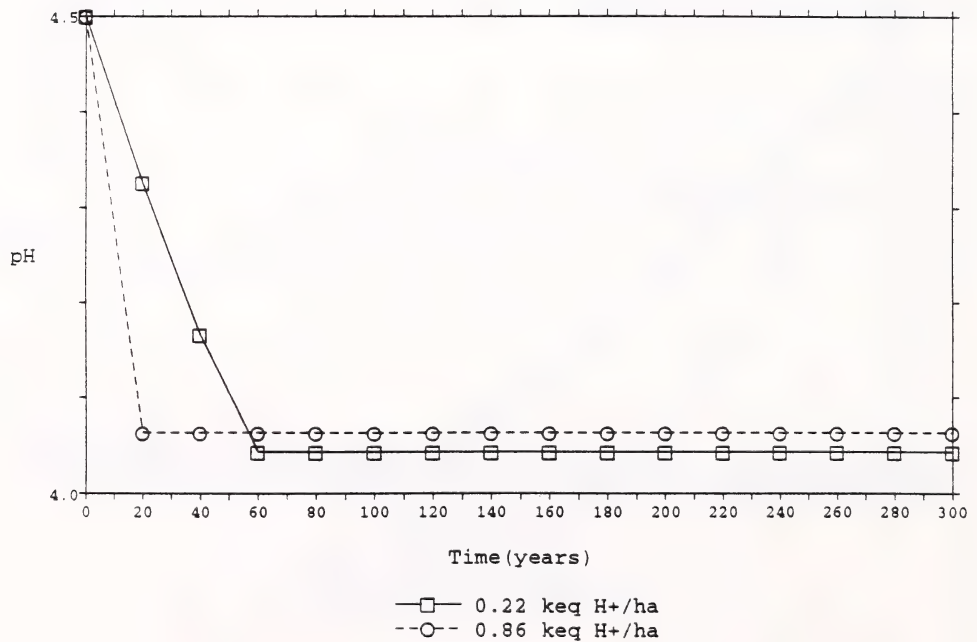


Figure 22. Base saturation (BS) changes for the Ft. McMurray site 2 soil.

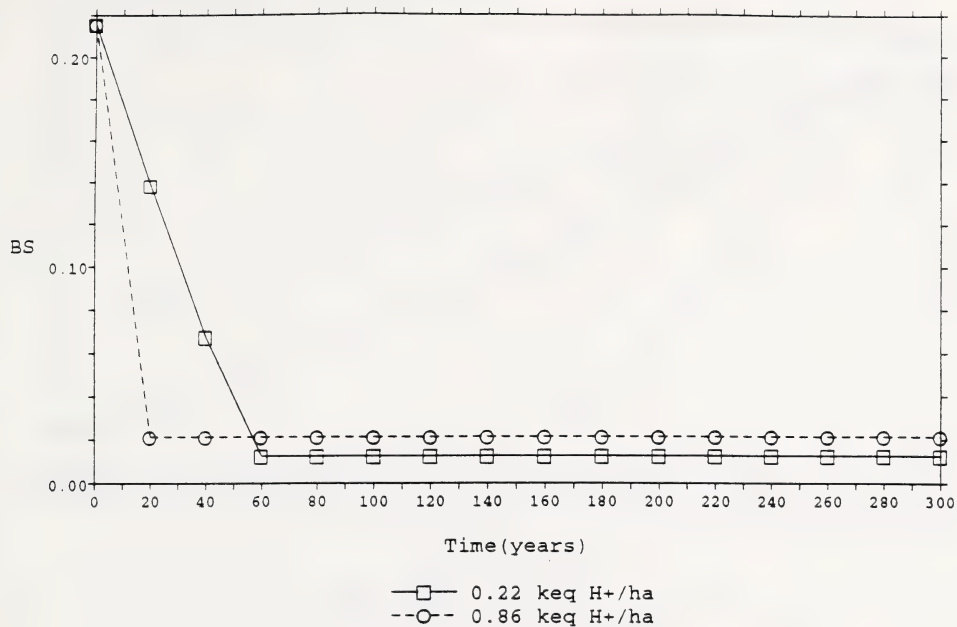


Figure 23. Soluble Al changes for the Ft. McMurray site 2 soil.

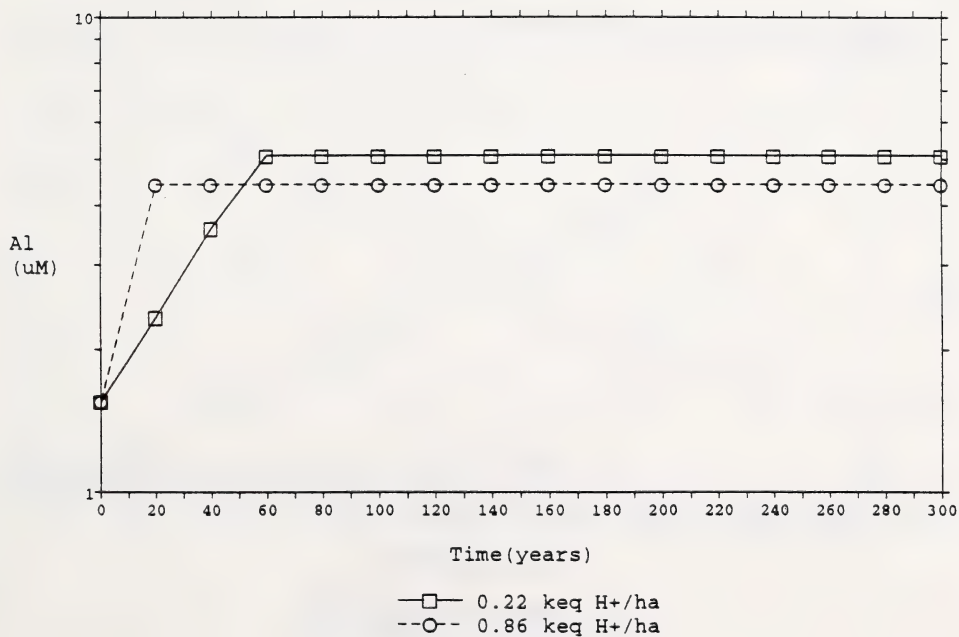


Figure 24. pH changes for the High Prairie site soil.

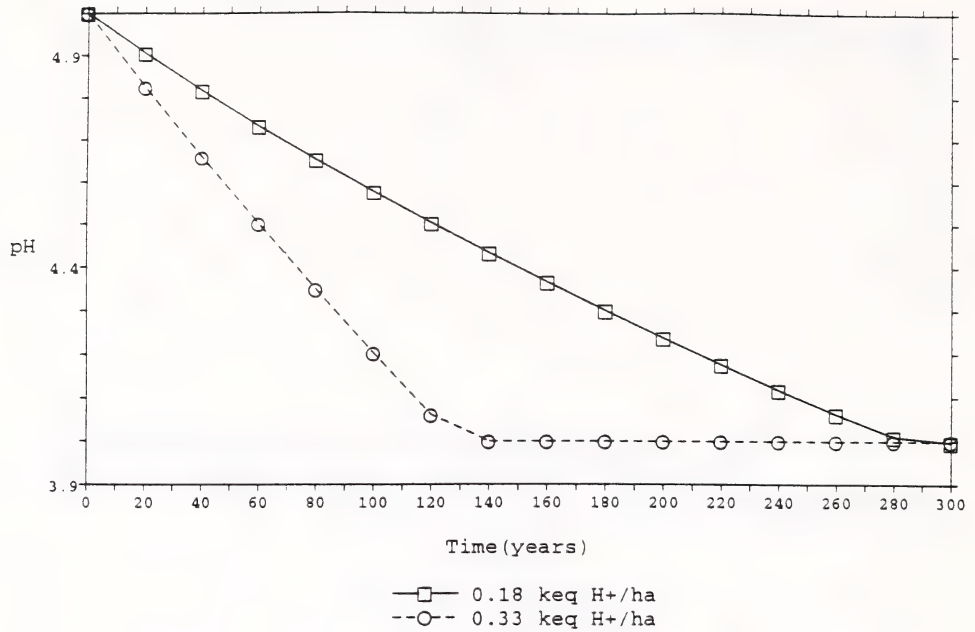


Figure 25. Base saturation (BS) changes for the High Prairie site soil.

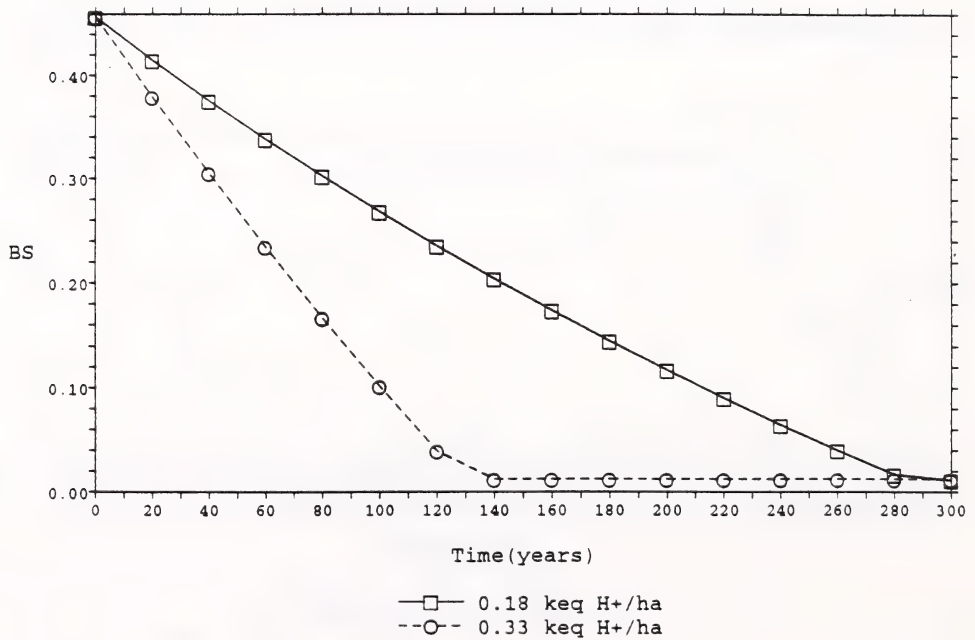


Figure 26. Soluble Al changes for the High Prairie site soil.

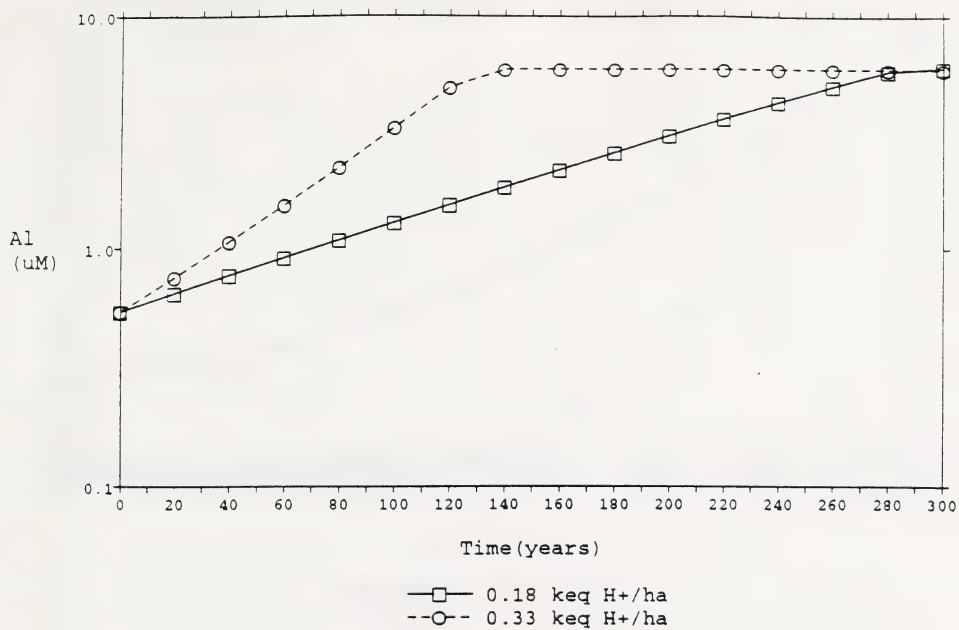


Figure 27. pH changes for the Cold Lake site soil.

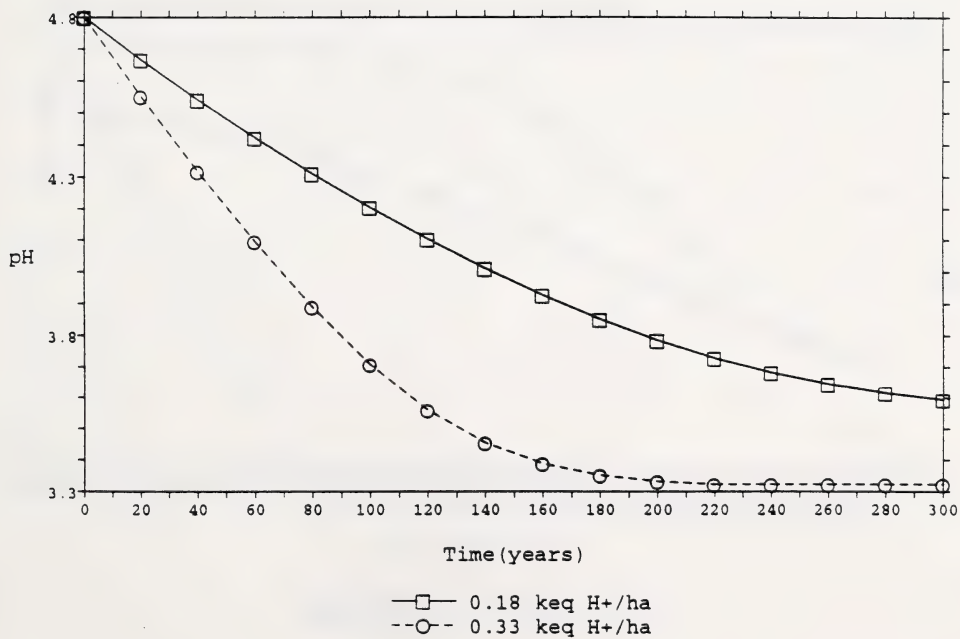




Figure 28. Base saturation (BS) changes for the Cold Lake site soil.

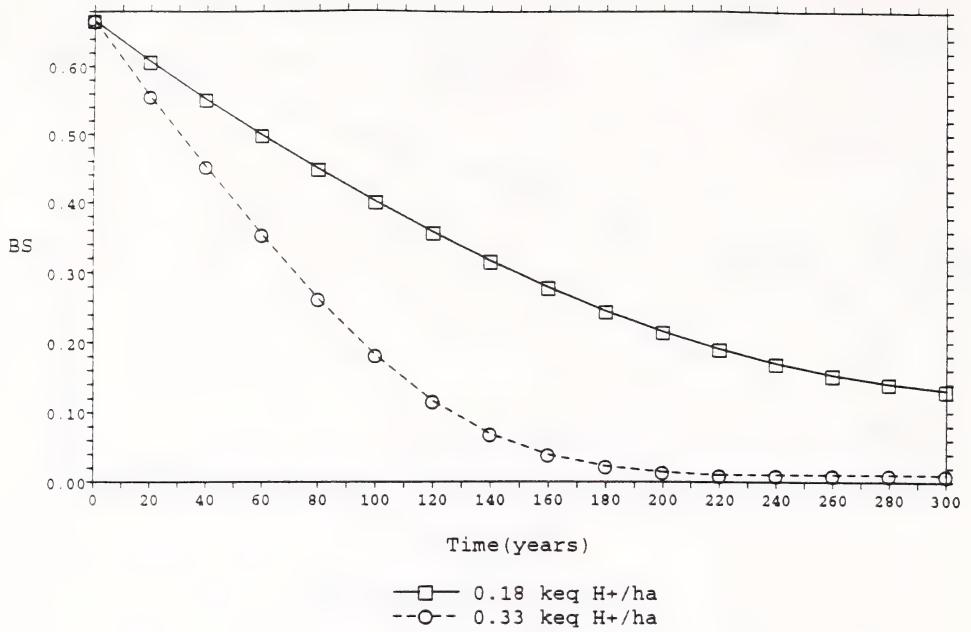


Figure 29. Soluble Al changes for the Cold Lake site soil.

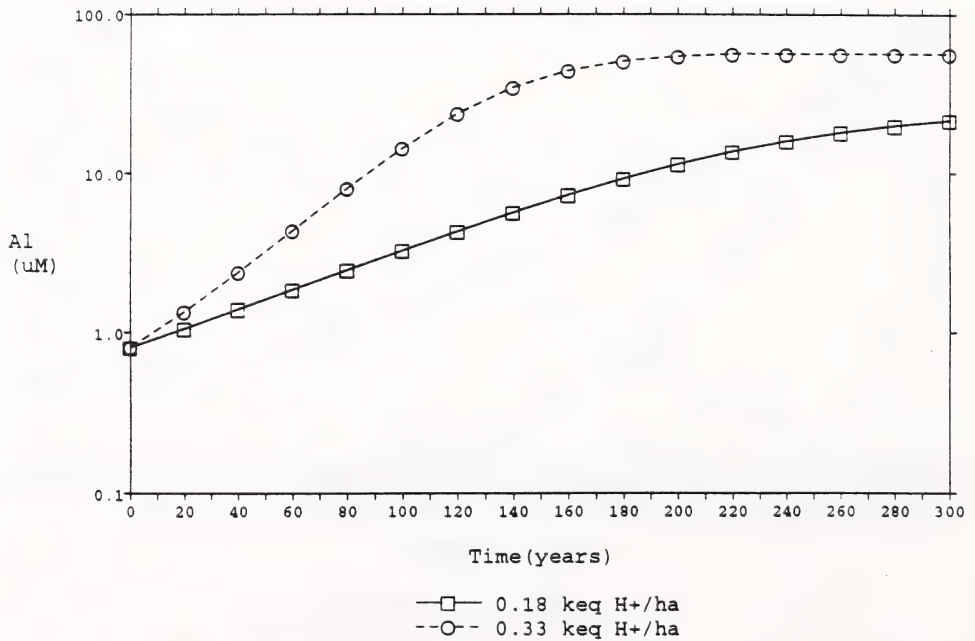


Figure 30. pH changes for the Bruderheim site soil.

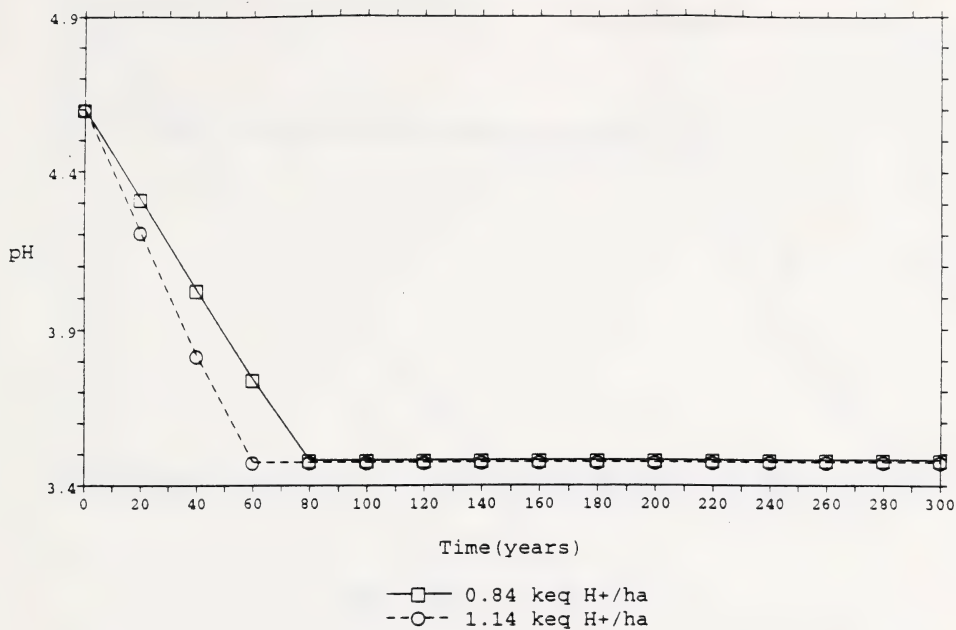


Figure 31. Base saturation (BS) changes for the Bruderheim site soil.

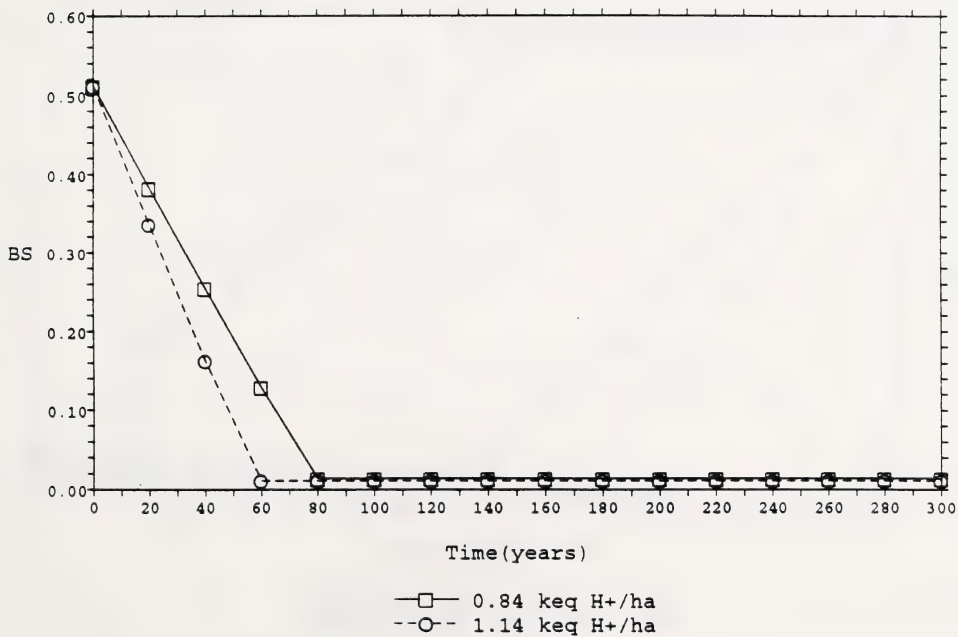


Figure 32. Soluble Al changes for the Bruderheim site soil.

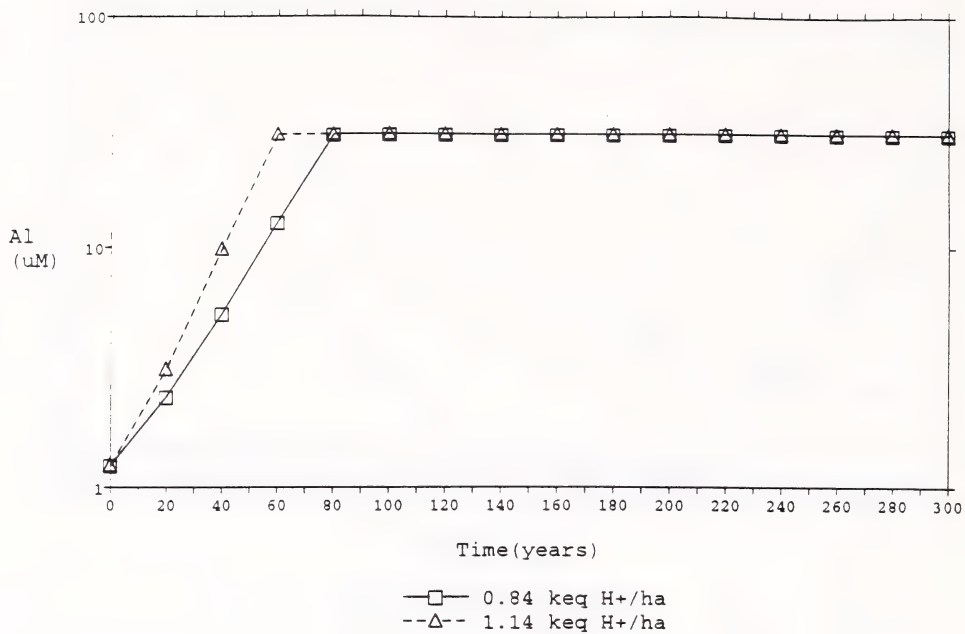


Figure 33. pH changes for the Devon site soil.

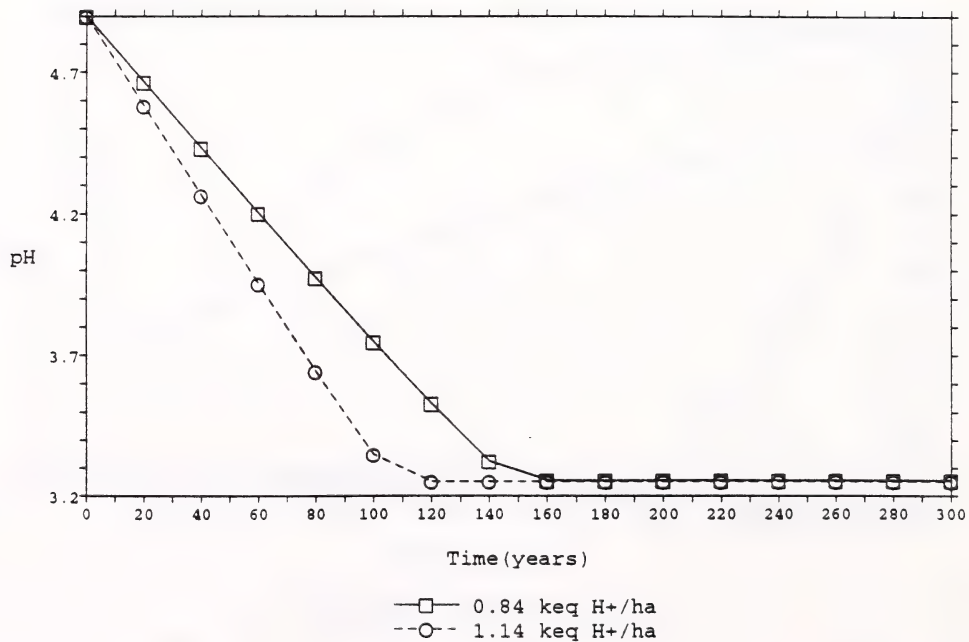


Figure 34. Base saturation (BS) changes for the Devon site soil.

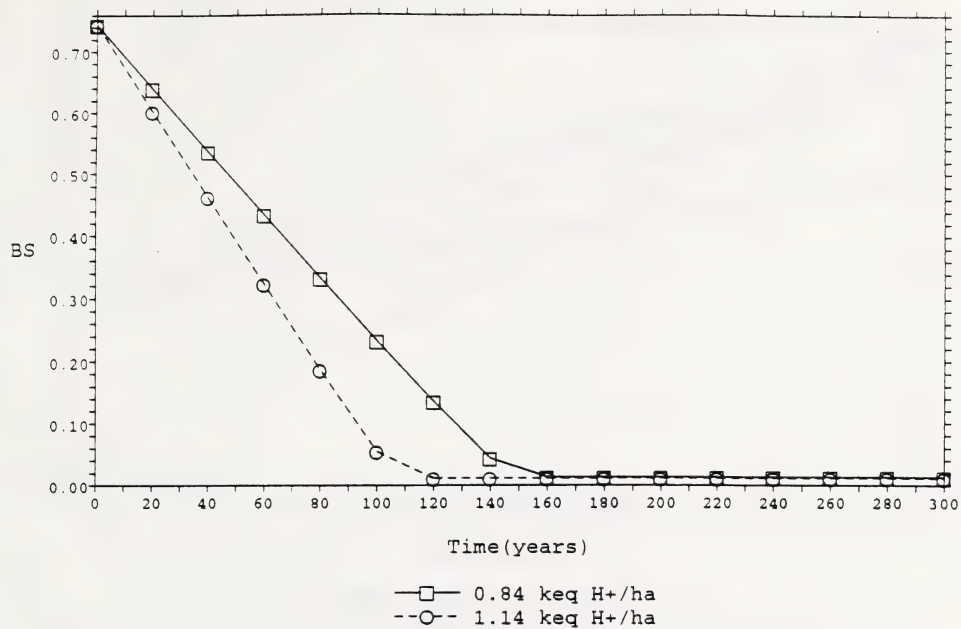


Figure 35. Soluble Al changes for the Devon site soil.

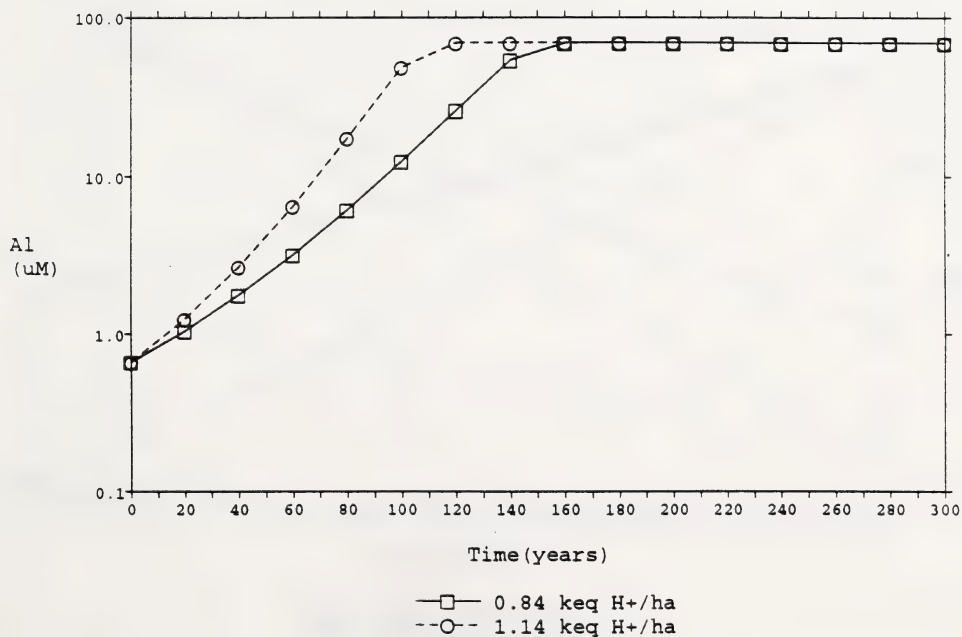


Figure 36. pH changes for the Rocky Mountain House site soil.

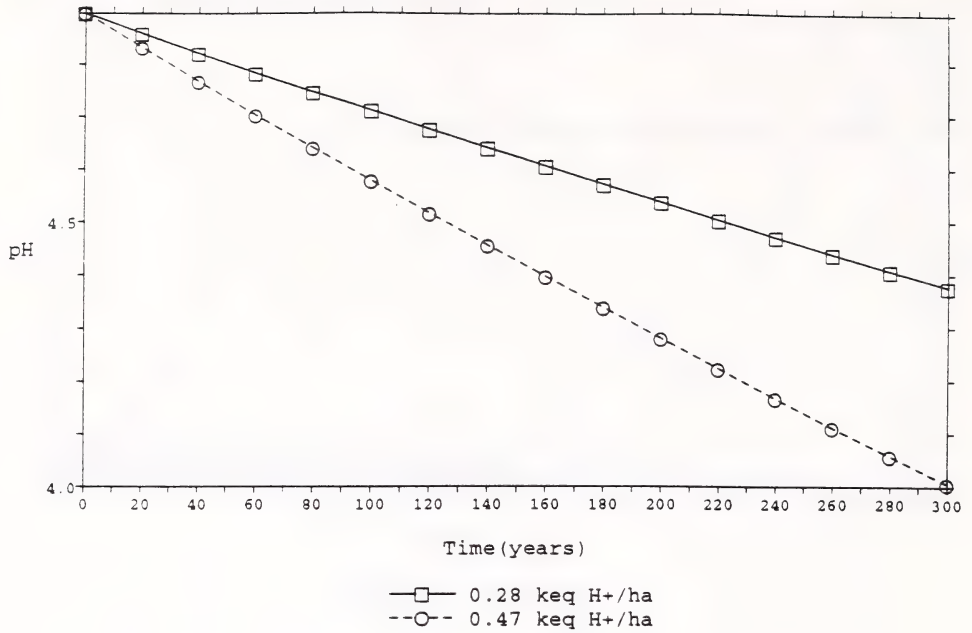


Figure 37. Base saturation (BS) changes for the Rocky Mountain House site soil.

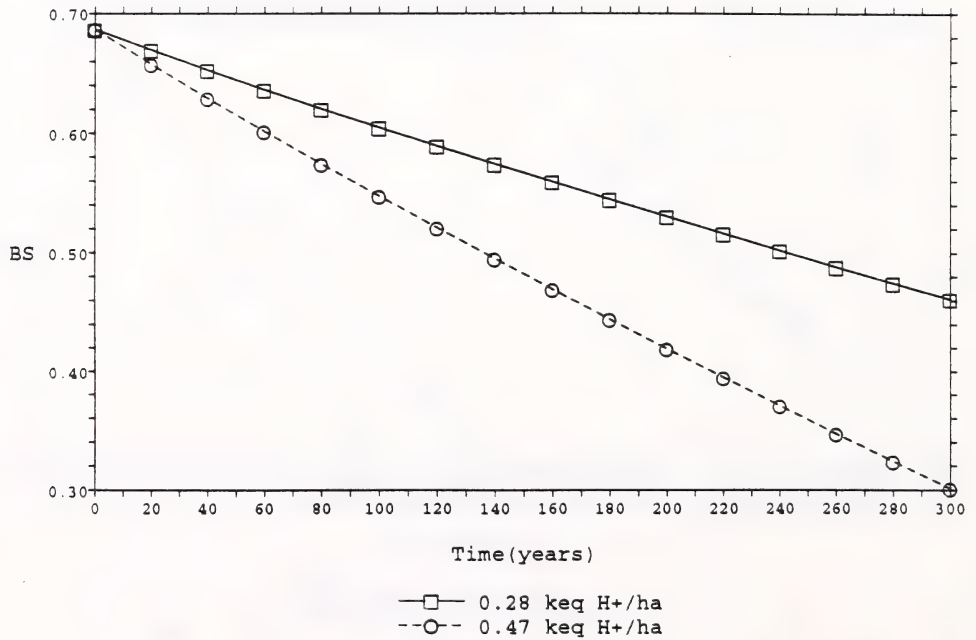




Figure 38. Soluble Al changes for the Rocky Mountain House site soil.

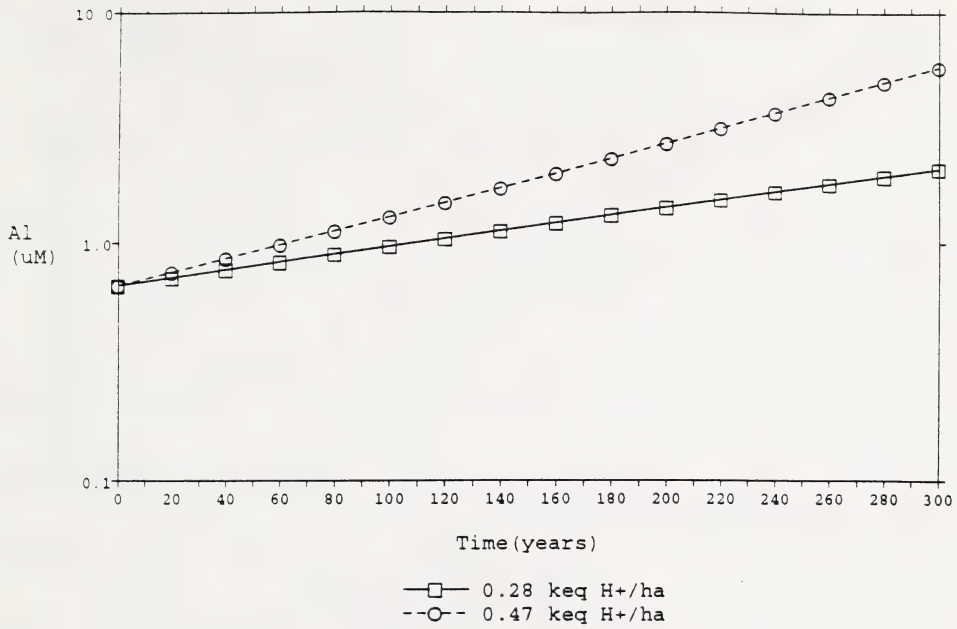


Figure 39. pH changes for the Twin Butte site soil.

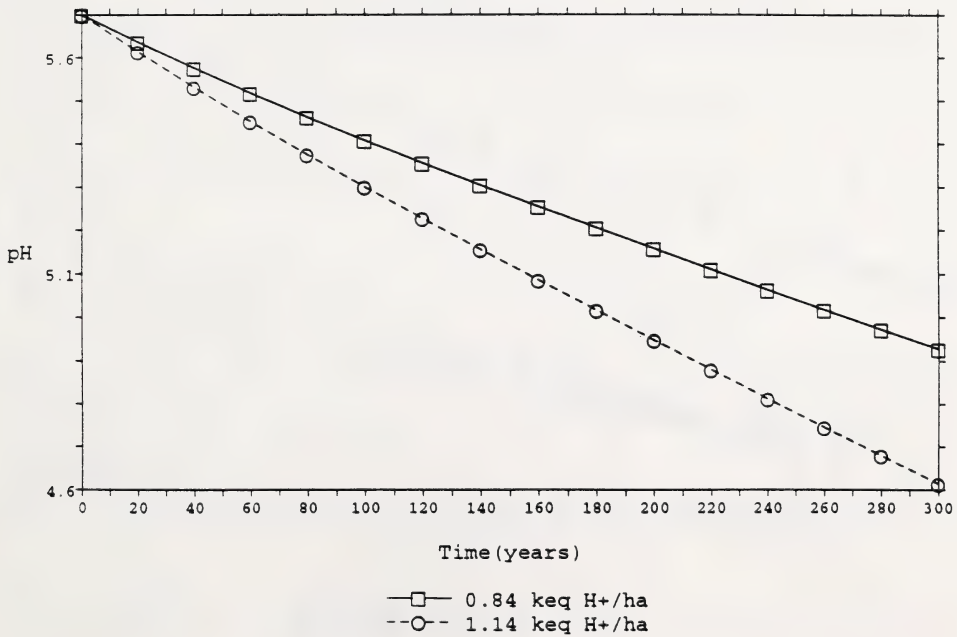


Figure 40. Base saturation (BS) changes for the Twin Butte site soil.

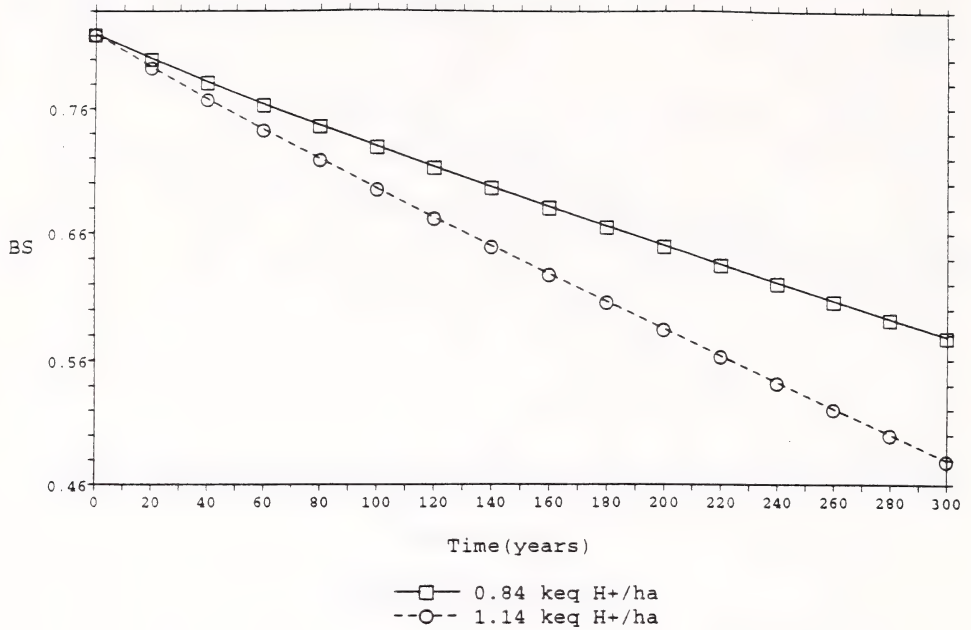


Figure 41. Soluble Al changes for the Twin Butte site soil.

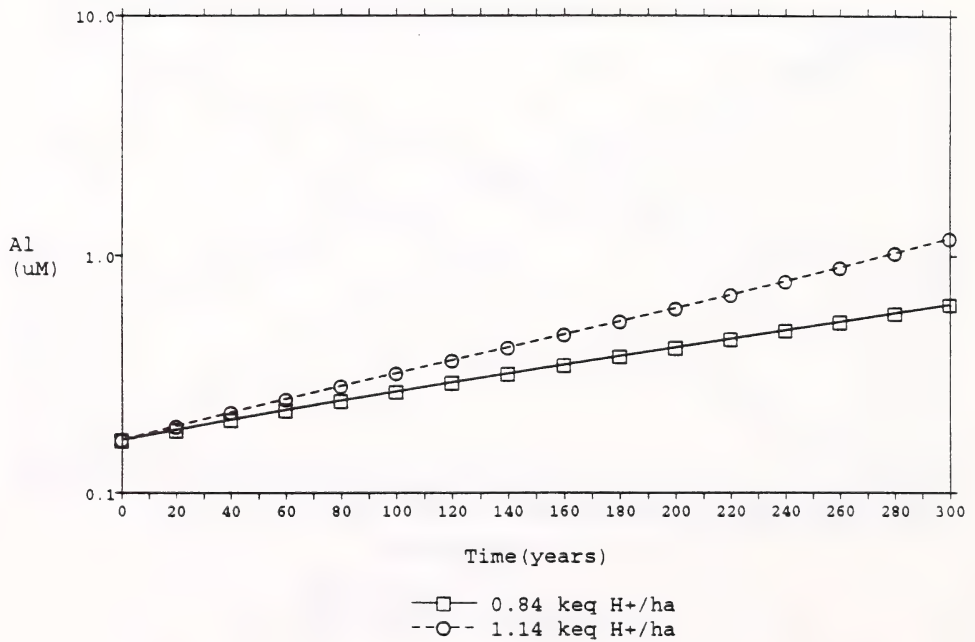


Figure 42. pH changes for the Esther site soil.

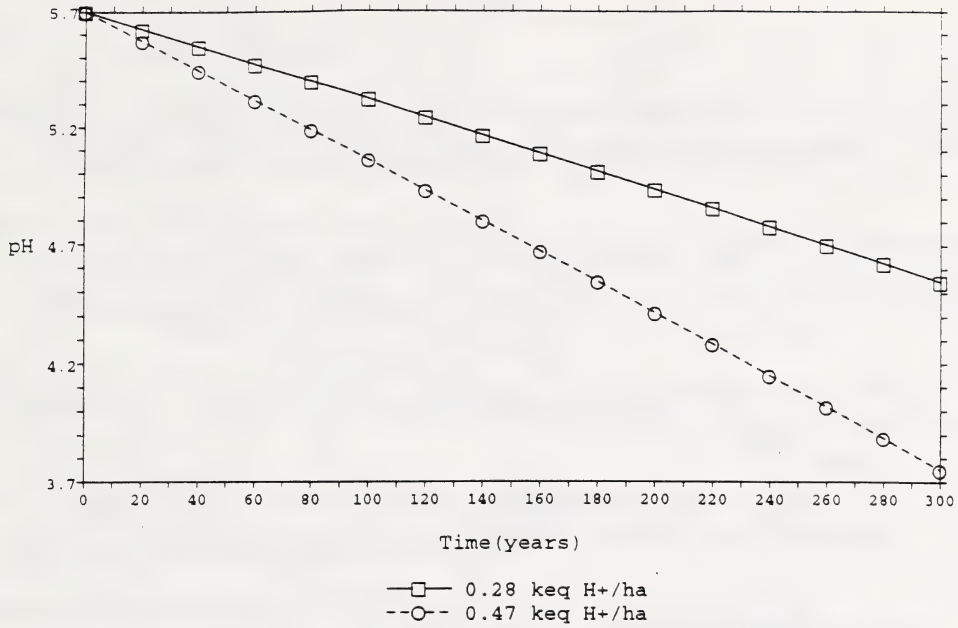


Figure 43. Base saturation (BS) changes for the Esther site soil.

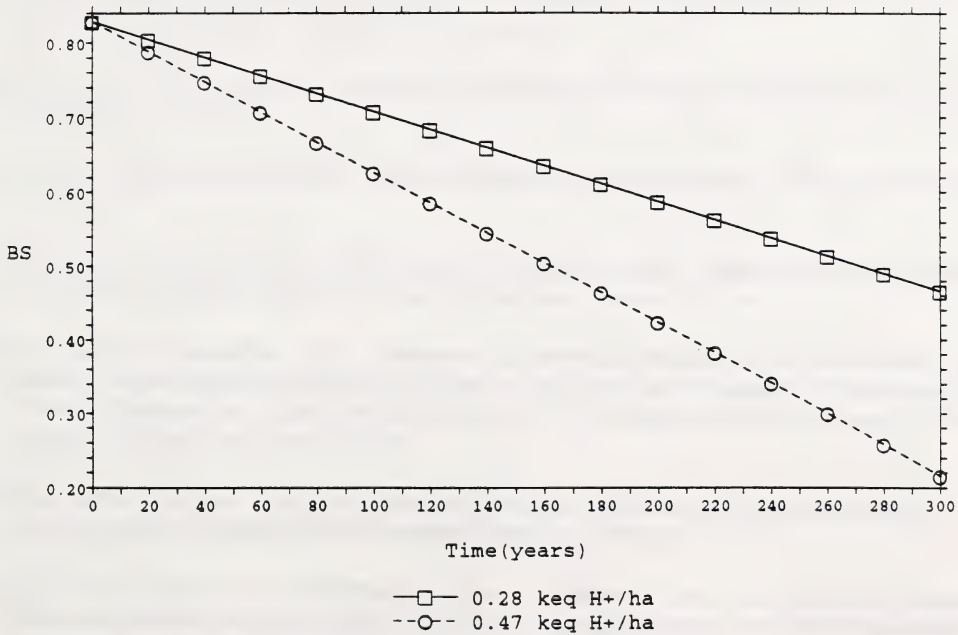
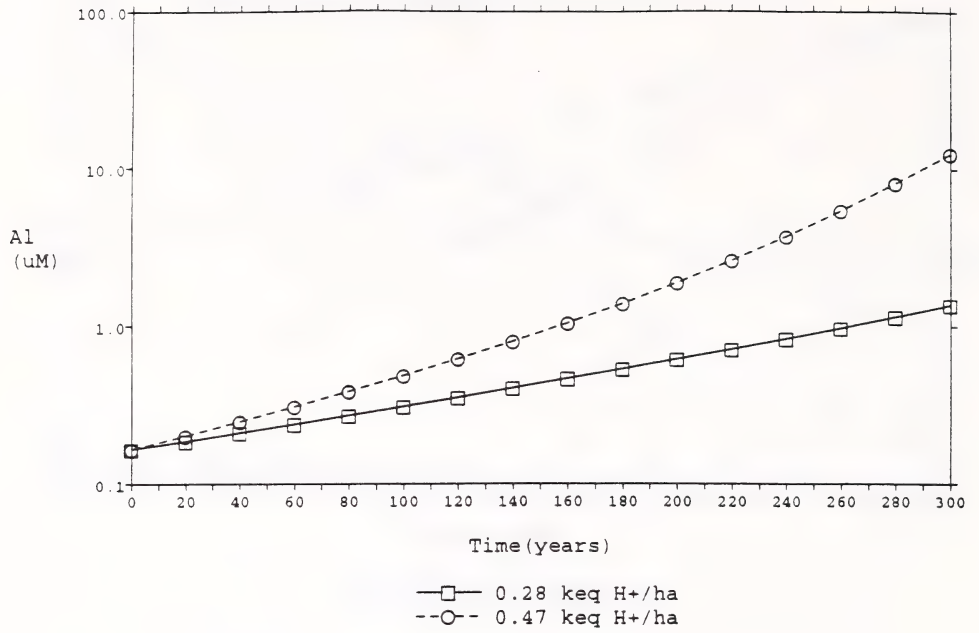


Figure 44. Soluble Al changes for the Esther site soil.



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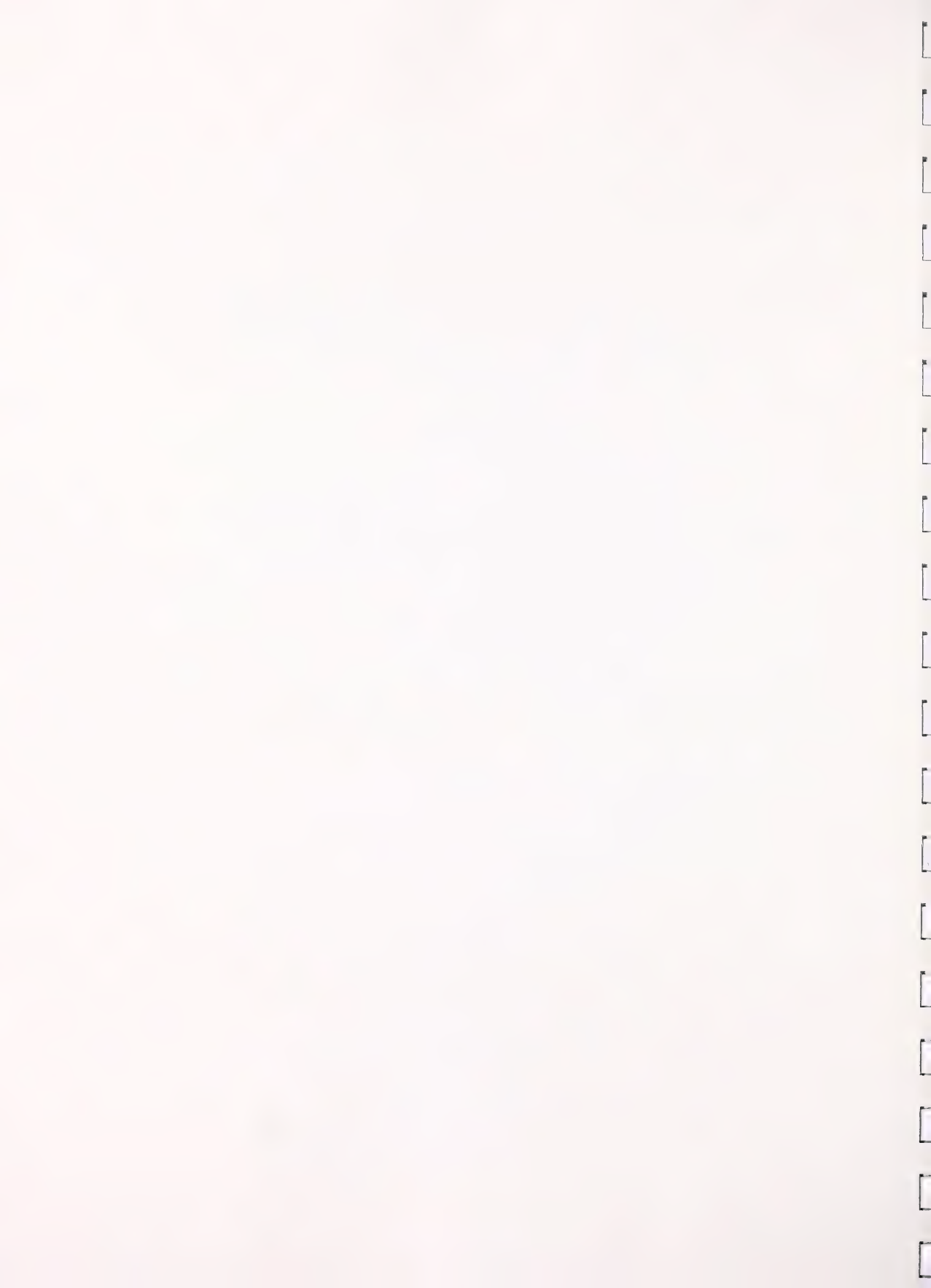
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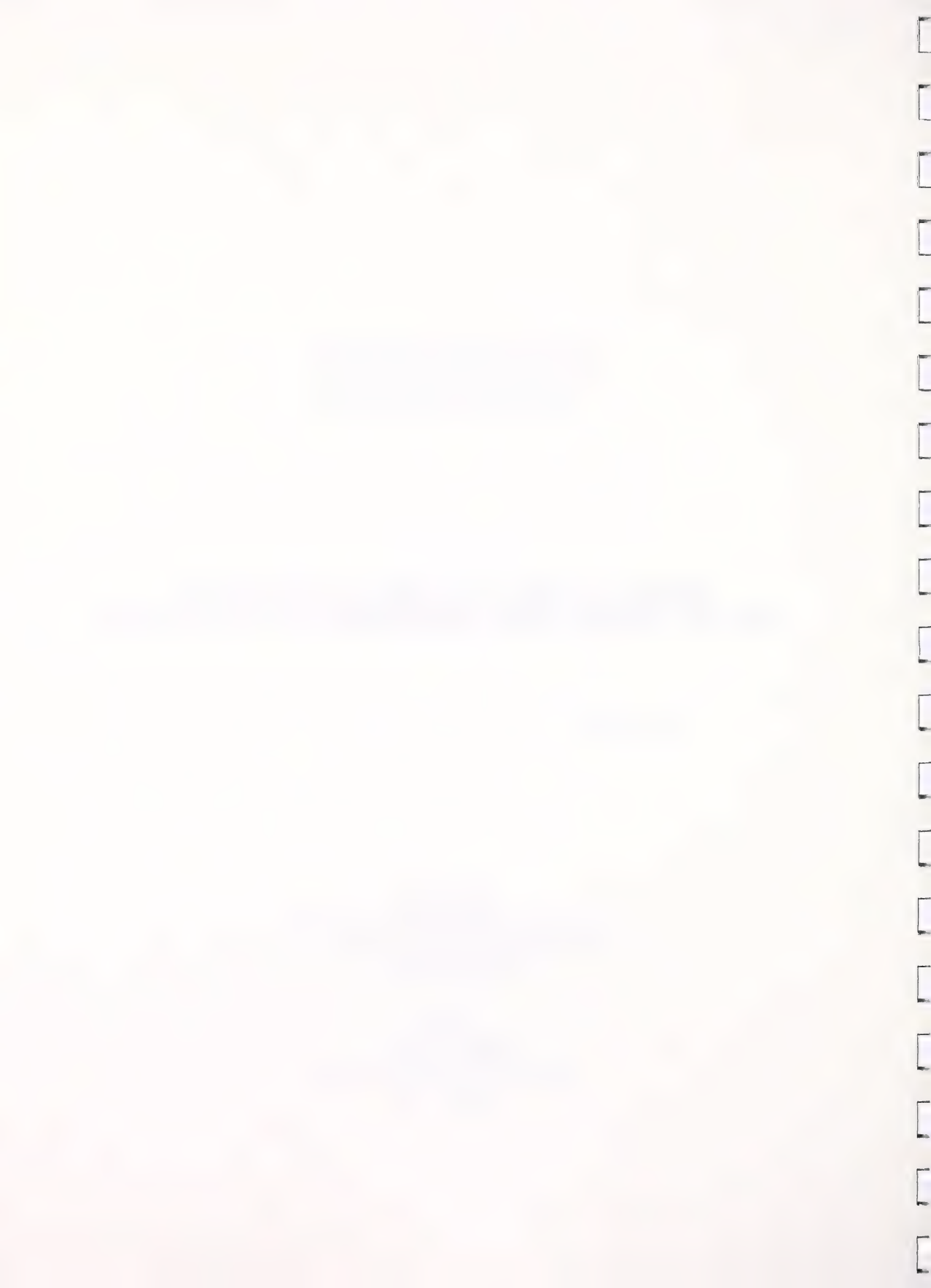




## SECTION 4

Protocol Method for Ambient Air Sampling with the  
Combined Annular Denuder-Filter Pack System





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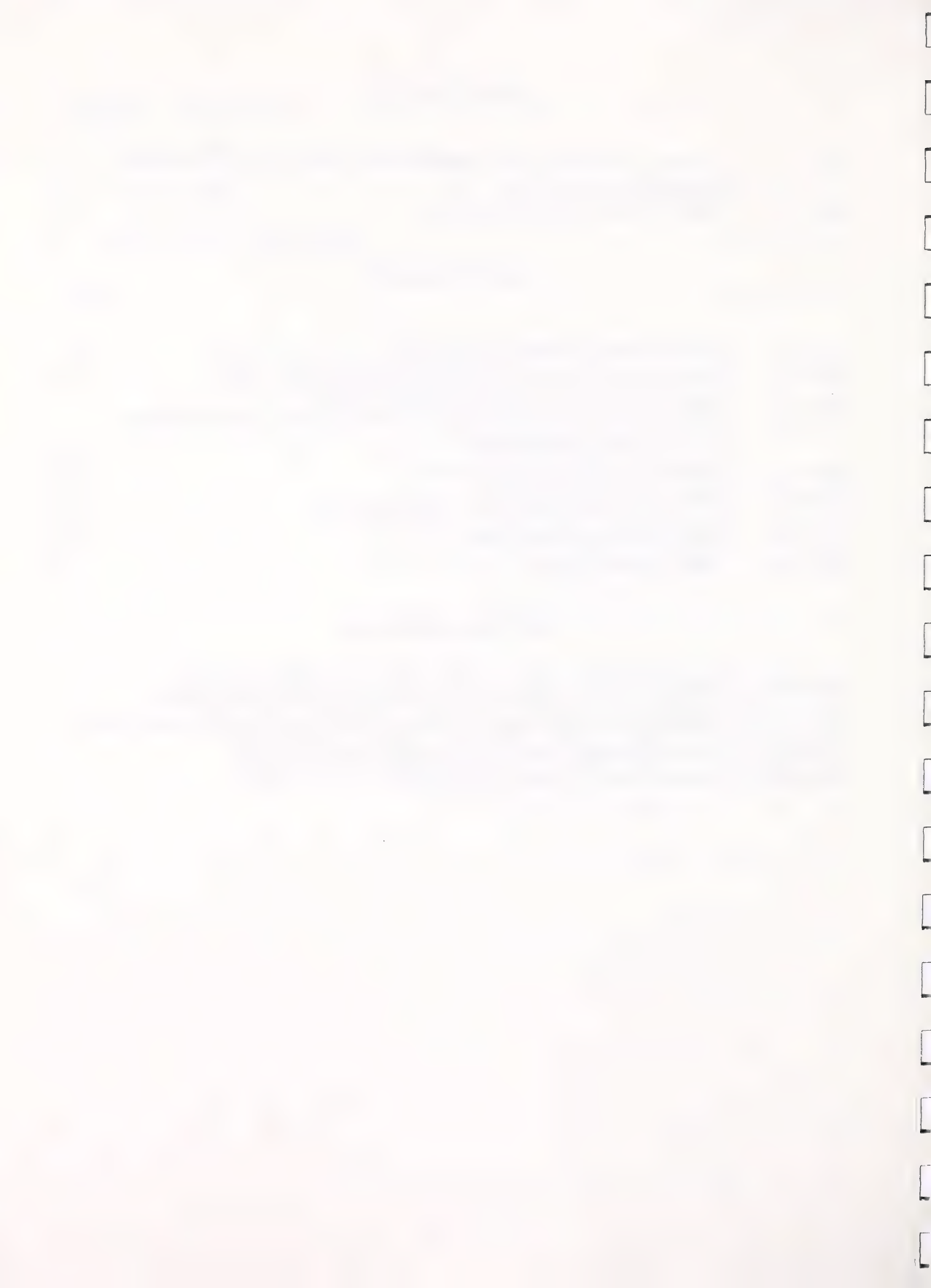
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### 1.1 Scope and Applications

The combined annular denuder filter pack system (AD-FP) is designed to separate and collect acidic gases, ( $\text{HNO}_2$ , and  $\text{HNO}_3$ ), basic gases ( $\text{NH}_3$ ), and fine particles from the ambient atmosphere. The collected gases and fine particles are chemically analyzed. By monitoring the atmospheric sampling rate the concentration of these pollutants in the atmosphere is determined. Sampling periods from a few hours to one week (or more) may be employed allowing low concentrations of pollutants such as those found at rural and remote locations to be monitored. Detection and maximum concentration limits are given in Table 1.

### 1.2 Summary of Method

The AD-FP system consists of a cyclone, a series of three annular denuder tubes and a filter pack which are assembled into a rigid housing (Figure 1). The unit is mounted on a sampling tower and connected to a vacuum pump, flow controller, and data logger which are contained in an air quality monitoring trailer. Ambient air is pulled through the unit by the vacuum pump with the flow being regulated and monitored by a mass flow controller. The data logger controls the start and length of the sampling period and records the flow through the unit. A Teflon cyclone at the inlet removes the coarse particles (i.e. particles with diameters of  $>2.5$   $\mu\text{m}$ ) before the sample passes to the annular denuders. Gases drawn through the annulus of the annular denuder tubes diffuse to a reactive surface and are captured. Fine particles, because of their momentum pass through the tubes and are collected on filters.

The annular denuder tubes are composed of two concentric glass cylinders with a 1.6 mm space between them (Figure 2). The glass walls of the annulus are etched to provide a surface on which chemicals, that absorb the gaseous species of interest, are coated. The first and second denuder tubes are coated with a mixture of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and glycerol to collect acid gases, sulphur dioxide ( $\text{SO}_2$ ), nitrous acid ( $\text{HNO}_2$ ), and nitric acid ( $\text{HNO}_3$ ). These are collected and analyzed by ion chromatography as sulphate ( $\text{SO}_4^{2-}$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ), respectively. The glycerol acts as a wetting agent facilitating reaction of the gases with the reactive surface. The third denuder tube in the series is coated with a mixture of citric acid

and glycerol and is used to collect ammonia ( $\text{NH}_3$ ). Ammonia is analyzed by ion chromatography.

Laminar flow is maintained within the annulus permitting fine particles (diameter  $<2.5 \mu\text{m}$ ) to pass through the tubes with negligible loss. These particles are collected with a two stage filter pack which contains a Teflon membrane filter followed by a nylon membrane filter. The fine particles of interest are principally acidic and/or ammonium sulphate and ammonium nitrate aerosol. The Teflon filter retains all the sulphate particulate matter. Under some conditions, a significant portion of the nitrate aerosol ( $\text{NH}_4\text{NO}_3$ ) on the Teflon filter can dissociate into  $\text{NH}_3$  and  $\text{HNO}_3$ . The nylon back-up filter captures the volatile nitrate produced, thus the two filters together capture all of the fine particle aerosol.

To prepare the unit for each sampling "run", the three annular denuder tubes are coated: two with  $\text{Na}_2\text{CO}_3$  (for acid gases), and one with citric acid (for ammonia). The filter pack is loaded with the Teflon filter and the backup nylon filter. The system consisting of the cyclone, three tubes, two tube-to-tube connectors and the filter pack are assembled into its rigid tubular housing prior to being placed in a shipping case for transport to the field. In the field, the unit is connected via flexible tubing to the pump/flow control unit with quick release connectors and is attached to a trolley which is raised to the sampling height on a ten metre tower.

Following each run, the unit is disconnected and transported in its shipping case to the laboratory. The assembly pieces are uncoupled, the denuder tubes and the filters are extracted with deionized water. The denuder tubes are then cleaned in preparation for the next run.

Table 1. Estimated Detection and Quantification Limits for the Annular Denuder-Filter Pack System

Detection Limits (ug/m <sup>3</sup> )	Sampling Period		
	1 hour	1 day	1 week
(a) gaseous species			
SO <sub>2</sub>	1.7	0.072	0.010
HNO <sub>3</sub>	0.93	0.039	0.006
HNO <sub>2</sub>	1.27	0.052	0.008
NH <sub>3</sub>	3.9	0.17	0.024
(b) particulate species			
SO <sub>4</sub> <sup>2-</sup>	0.31	0.013	0.002
NO <sub>3</sub> <sup>-</sup>	2.1	0.086	0.012

Quantitation Limits (ug/m <sup>3</sup> )	Sampling Period		
	1 hour	1 day	1 week
(a) gaseous species			
SO <sub>2</sub>	5.5	0.23	0.032
HNO <sub>3</sub>	4.1	0.17	0.024
HNO <sub>2</sub>	5.6	0.24	0.034
NH <sub>3</sub>	17.0	0.70	0.101
(b) particulate species			
SO <sub>4</sub> <sup>2-</sup>	0.96	0.039	0.006
NO <sub>3</sub> <sup>-</sup>	6.3	0.27	0.038

Samples analyzed by ion chromatography. Detection limits based on a sampling rate of 7.1 Lpm and are taken as 4.65 times the standard deviation in the blank values. Quantitation limits are 14.1 times the standard deviation in the blanks. (Kirchmer, C.J. Quality control in water analysis. *Environ. Sci. and Technol.* 17, 174A-181A, 1983.)

### 1.3 Definitions

This protocol uses no definitions which are unique to this document.

### 1.4 Interferences

Less than 5 percent of the nitrogen dioxide ( $\text{NO}_2$ ) in the ambient atmosphere being sampled will be retained by each of the two  $\text{Na}_2\text{CO}_3$  coated denuder tubes as nitrite. The retained nitrite would interfere in the measurement of nitrous acid, but the second  $\text{Na}_2\text{CO}_3$  coated denuder tube provides the small correction necessary in the calculation of nitrous acid concentrations.

### 1.5 Personnel and Training Requirements

The AD-FP does not require any unusual degree of skill for use. Competent personnel capable of performing routine laboratory procedures should be capable of learning AD-FP operation procedures. The coating, assembly, and extraction of annular denuders are skills which are not readily demonstrated in written procedures. For this reason, it is highly recommended that the use of the AD-FP be demonstrated by experienced personnel.

### 1.6 Facilities Requirements

Laboratory facilities with better than average air quality and standards of cleanliness are required.

### 1.7 Chemical Hazards

#### 1.7.1 Methanol

**WARNING Flammable Liquid.** Keep away from heat, sparks, or open flame.

**WARNING Toxic Liquid.** May be fatal or cause blindness if swallowed, inhaled, or absorbed through the skin. Use adequate ventilation and protective clothing. See WHMIS material safety data sheet for additional information.

#### 1.7.2 Ascarite

**WARNING Poisonous, corrosive solid ( $\text{NaOH}$  coated).** Harmful if inhaled. Causes severe burns. May be fatal if swallowed. Use adequate ventilation and protective clothing. See WHMIS material safety data sheet for additional information.



## 1.7.3 Drierite

WARNING Poisonous solid. May be fatal if swallowed. Causes irritation. Do no breath dust. Use adequate ventilation. Wash thoroughly after handling. See WHMIS material safety data sheet for additional information.

1.8 Apparatus (Figure 1)

Items 1.8.1 through 1.8.9 constitute the AD-FP unit, items 1.8.10 through 1.8.13 the field support system, and items 1.8.14.1 through 8.11.14.12 the laboratory support system.

## 1.8.1 Teflon Cyclone Assembly

The cyclone is constructed of PFE Teflon and is based on the design of Smith and Wilson and is similar to that used by the United States EPA (Smith, W. B. and R. R. Wilson, A Five-Stage cyclone system for in-situ sampling. *Environ. Sci. and Technol.* 13, 1387-1392, 1979). The particle size cut point of the cyclone depends upon the sampling rate. With a flow rate of 7.1 Lpm, the cyclone shown in Figure 2. will pass 87% of the particles of 2.0 um in diameter and 100% of particles 1.0 um in diameter, or smaller. It will retain 85% of particles of 3.0 um in diameter and 95% of those particles of 4.0 um and larger.

1.8.1.1 Teflon cyclone body.

1.8.1.2 Teflon inlet, 1/4" pipe to 1/4" connector (1).

1.8.1.3 Teflon outlet, 1/4" pipe to 1/16" tube connector (1).

1.8.1.4 Teflon tubing, 1/16", 12".

1.8.1.5 Teflon connector, 1/16" tube to 1/4" tube.

1.8.1.6 Quick connect, 1/4".

1.8.2 Annular denuder tubes, two with conical ends and one with flat ends per sampling unit (Figure 2).

1.8.3 Teflon couplers (2).

1.8.4 Teflon 3/4" front ferrules (6). Note -- must be Swagelock as other suppliers' Teflon ferrules are not suitable for this application.

1.8.5 Teflon 3/4" back ferrules (6).

1.8.6 Brass 3/4" pipe to tube connector (5). To be machined to a full bore.

1.8.7 Teflon filter holder (1).

1.8.7.1 Teflon filter holder body.



- 1.8.7.2 Teflon filter support discs (2).
- 1.8.7.3 Brass 3/8" pipe to tube connector (1).
- 1.8.8 Unit support case.
- 1.8.8.1 Tubular support.
- 1.8.8.2 Nylon bulkhead fitting, 3/8" (1).
- 1.8.8.3 Quick connector, 3/8" (1).
- 1.8.8.4 Polyethylene tubing, 3/8", 12".
- 1.8.8.5 Tube to tube reducing connector 3/8" by 1/2" (1).
- 1.8.9 Vacuum tubing. Industrial grade braided poly vinyl tubing (Tygon), 1/2" outside diameter, 50 ft; 1/4" outside diameter, 50 ft.
- 1.8.10 Flow control system.
- 1.8.10.1 Mass flow controller with ability to control flow of 7.1 Lpm (Tylan FC 262, or Hastings).
- 1.8.10.2 Fitting, 3/8" pipe to 1/2" tube.
- 1.8.10.3 Vacuum pump with 1/2" pipe inlet (GAST Model 0822-V103-G271X, oil free, or similar).
- 1.8.10.4 Fitting, 1/2" pipe nipple.
- 1.8.10.5 Fitting, 1/2" pipe female "T".
- 1.8.10.6 Fitting, 1/2" pipe male to 3/8" tube (2).
- 1.8.10.7 Fitting, 3/8" tube to 1/2" tube.
- 1.8.10.8 Fitting, cap for 3/8" tube fitting.
- 1.8.10.9 Fitting, cap for 1/4" tube fitting.
- 1.8.11 Case for shipping sampling units (2).
- 1.8.12 Standard flow calibration equipment.
- 1.8.13 Coating and extracting cups (8).
- 1.8.14 Manifold for drying denuder tubes.
- 1.8.15 Drying train including Ascarite, drierite, and silica gel drying units.
- 1.8.16 Volumetric flask, 50 mL and 2 L for preparation and storage of coating solutions (2).
- 1.8.17 Graduated cylinders, 50 mL borosilicate glass or polyethylene.
- 1.8.18 Graduated cylinder, 10 mL, 50 mL, and 500 mL borosilicate glass.

- 1.8.19 5 mL pipette (class A) or automatic pipette (recommended).
- 1.8.20 10 mL pipette (class A) or automatic pipette.
- 1.8.21 Disposable Pasteur pipettes.
- 1.8.22 Filter forceps.
- 1.8.23 20 mL Teflon vials with screw caps (TUF-TAINERS) (48).
- 1.8.24 Ultrasonic cleaning bath.
- 1.8.25 Stainless steel test tube rack.
- 1.8.26 Rack for holding filter packs during assembly.

## 1.9 Laboratory Equipment & Supplies

- 1.9.1 Teflon filters. Zefluor (PTFE) membrane filters 47 mm diameter with a 2  $\mu$ m pore size.
- 1.9.2 Nylon filters. Nylasorb membrane filters 47 mm in diameter with a 1  $\mu$ m pore size. Gelman number 66509, or equivalent.

NOTE: considerable contamination has been found in the filters produced by some manufacturers and all lots should be tested for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  prior to use.

- 1.9.3 Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 99.995%.
- 1.9.4 Sodium bicarbonate ( $\text{NaHCO}_3$ ).
- 1.9.5 Methanol. ACS reagent grade. SEE SAFETY WARNING section 1.7.1.
- 1.9.6 Glycerol. (Glycerin) ACS reagent grade.
- 1.9.7 Citric acid (monohydrate). Sigma gold grade.
- 1.9.8 Deionized water. ASTM type 1 water. NOTE: great care should be exercised in obtaining a supply of deionized water free from  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  contamination.
- 1.9.9 Gloves. Polyethylene disposable.
- 1.9.10 Zero air. A supply of compressed clean air, free from particles, water vapor,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{HNO}_2$ . Commercial cylinder zero air is available and medical grade air is available.
- 1.9.11 Analytical balance.
- 1.9.12 Hot plate.
- 1.9.13 Plastic bags.
- 1.9.14 Cylinder regulator.

- 1.9.15 2 L polypropylene bottle with screw cap.
- 1.9.16 Labels, waterproof.
- 1.9.17 Parafilm.
- 1.9.18 Spatula.
- 1.9.19 Weighing papers.
- 1.9.20 Split Teflon tubing, ¼".

## 1.10 Preparation of Sampling Unit

- 1.10.1 Cleaning of annular denuder system.
- 1.10.1.1 Cleaning of parts during normal use.

The cyclone inner surface should be wiped with a paper tissue to remove particles. The cyclone and filter pack should be placed in deionized water in an ultrasonic cleaning bath for 5 minutes to remove contamination as required. The parts should then be rinsed with deionized water and allowed to air dry. Denuder tubes should be boiled in deionized water, rinsed several times, and allowed to air dry in the stainless steel test tube rack.

### 1.10.2 Preparation of Coating Solutions

- 1.10.2.1 Preparation of  $\text{Na}_2\text{CO}_3$  denuder coating solution.

Weigh 1 g of  $\text{Na}_2\text{CO}_3$  into a clean 50 mL volumetric flask and add 1 g of glycerol using a disposable pipette. With a graduated cylinder add 25 mL of deionized water and mix until the  $\text{Na}_2\text{CO}_3$  is totally dissolved. Bring the total volume to 50 mL by adding methanol. Mix thoroughly, label, and store at room temperature.

- 1.10.2.2 Preparation of citric acid denuder coating solution.

Weigh 1.0 g of citric acid into a 50 mL volumetric flask. Add 1 g of glycerol using a disposable pipette. With a graduated cylinder, add 25 mL of distilled water. Mix thoroughly until the citric acid is dissolved. Bring the volume to 50 mL by adding methanol. Mix thoroughly, label, and store at room temperature.

### 1.10.3 Coating Denuder Tubes

NOTE: Each set of tubes consists of two  $\text{Na}_2\text{CO}_3$  coated tubes (one of which has two flat ends), and one citric acid coated tube. The tubes have serial numbers. The citric acid tubes are kept separately from the  $\text{Na}_2\text{CO}_3$  tubes. Two extra sets of each type are coated whenever sampling sets are prepared. These extra tubes are used as laboratory and field blanks.

1. Put on clean plastic gloves. (Note: Fisher brand polyethylene gloves are lowest in sulphate and latex gloves are lowest in chloride contaminants.)
2. Using a pipette, place 5 mL of the coating solution in the recessed end of the annular denuder tube cup.
3. Insert the denuder tube into the cup and seal by hand-tightening the top of the cup.
4. Place a second cup on the other end of the tube and seal.
5. Rotate so as to distribute the solution evenly within the annulus of the tube ensuring that no air bubbles prevent even coating. Remove one cup, pour out and discard excess solution.
6. Remove second cup and place the tube in a stainless steel rack for 5 minutes to allow excess coating solution to drain.
7. Repeat for each tube.

#### 1.10.4 Drying of Denuder Tubes

After the tubes have been coated, they must be dried to leave a uniform coating.

Denuders are dry when they change from a translucent to a uniformly frosted appearance.

1. Adjust air flow through drying manifold to 2 to 3 L/min.
2. Remove tubes from stainless steel rack and insert in manifold.
3. Allow clean air to flow through the tubes for several minutes (until about 2/3 of each tube has changed appearance).
4. Reverse ends of the tubes on the manifold and allow air to flow for several more minutes until the tubes are uniformly opaque.
5. Remove the tubes from the manifold and seal in a clean plastic bag until ready for assembly into the sampling units.

#### 1.10.5 Filter Pack Preparation

1. Put on clean plastic gloves (see note 1.10.3).
2. Place filter packs in rack.
3. Unscrew the Teflon ring and remove the ring, the upper assembly, and the upper filter support. Lay the pieces removed on clean Kimwipes. The lower body assembly and filter support ring remain in the rack.



4. Using clean filter forceps, place a nylon filter on the lower filter support. (NOTE: Make sure that the filter is separated from the paper dividers and that a divider does not get put into the filter pack along with the filter.)
5. Place the second filter support on top of the nylon filter so that the filter is sandwiched between the two supports.
6. Using clean filter forceps, place the Teflon filter on the upper filter support.
7. Place the upper assembly on the filter making sure that the filters are in place and all parts are correctly aligned.
8. Place the large Teflon ring over the assembly and tighten by hand.

#### 1.10.6

##### Sampler Assembly

1. Remove the denuder tubes from their plastic bags (two  $\text{Na}_2\text{CO}_3$  tubes and one citric acid tube per set) and lay all the AD-FP parts on a clean surface. The cyclone should be disassembled.
2. Insert the cone shaped end of the first  $\text{Na}_2\text{CO}_3$  tube into the upper part of the cyclone and hand tighten the connector.
3. Insert the flat end of the tube into a coupling unit ensuring that the fitting at the end of the tube slides into the matching notches in the coupling unit.
4. Tighten the nut on the coupling unit by hand and snug with a wrench. CAUTION -- DO NOT OVERTIGHTEN.
5. Place the second  $\text{Na}_2\text{CO}_3$  tube into the coupling unit, making sure that the Teflon spacer at the end of the tube seats properly in the coupling unit notches, and tighten.
6. Connect the second tube to the flat end of the citric acid tube with a coupling unit, again ensuring that the tube is properly seated before tightening the nut.
7. Slide the assembled filter pack onto the citric acid tube, make sure it is seated properly, and tighten.
8. Assign a sample-run ID and record the serial numbers of the first, second, and third denuder tubes in the laboratory notebook.



9. Attach the vacuum tube, which passes through the cap of the housing to the filter pack. Tighten the 3/8" brass fitting with a wrench.
10. Slide the assembled unit into the housing so that the hexagon part of the assembly projects through the bottom of the housing unit.
11. Screw the bottom part of the cyclone to the part of the cyclone which projects from the bottom of the housing.
12. Slide the cap on the top of the assembly into place and hand tighten the nylon nut in the cap.
13. Cap the cyclone inlet and the filter outlet.
14. In the laboratory notebook record the unit number on the housing, the expected date, time, and duration of the sampling run.
15. Place the unit in the shipping case for transport to the field.
16. Record date and time the sampling unit is shipped, name of shipper, and manifest number.

## 1.11 Field Operation

### 1.11.1 Sampler Location

The sampling site should conform to the criteria of Alberta Environment for the type of terrain and distance from pollutant sources (including farm livestock) and obstructions such as buildings and trees. (See Appendix G).

### 1.11.2 Sampler Startup

1.11.2.1 With the vacuum pump running, cycle the control unit to test the functioning of the valves and to ensure that the correct unit is online.

1.11.2.2 Attach a flow meter to the vacuum line unit and compare the flow rate to that of the mass flow controller in the trailer.

1.11.2.3 If the flow rate does not correspond, check the calibration of the mass flow controller and adjust if necessary.

1.11.2.4 Remove the AD-FP unit from the shipping case and mount on the bracket attached to the tower trolley. Remove the caps on the unit and attach the vacuum line.

1.11.2.5 Check the flow at the cyclone inlet with a flow meter. If the inlet flow rate does not correspond to the mass flow meter, remove the unit from the housing and eliminate leaks by making sure all parts are properly seated and nuts tightened, and then reinstall.

1.11.2.6 Record the date and time of installation in the field log along with unit number, flow rate, notes regarding any adjustments to flow, difficulties encountered during installation, or comments regarding the condition of the site or the sampling units.

### 1.11.3 Sampler Removal

1.11.3.1 Note the date, time and unit number in the field log book.

1.11.3.2 Attach a flow meter to the inlet of the cyclone, cycle the controller to obtain flow through the unit and record the flow in the field log book.

1.11.3.3 Compare the flow with that recorder by the data logger and return the sampling controller to the correct cycle.

1.11.3.4 Disconnect the vacuum line and cap the inlet and outlet of the unit and the end of the vacuum line.

1.11.3.5 Note any observations about the condition of the site or the sampling unit in the field log book.

## 1.12 Sampler Disassembly and Extraction

### 1.12.1 Sampler Disassembly (performed in the laboratory)

1. Inspect and note any damage or loose fittings.
2. Record the unit number, date and time received, and the date and time disassembled in the laboratory notebook. Check the actual and expected sampling periods to ensure that they correspond.
3. Carefully remove the sampling unit from the shipping case and lay on a clean, flat surface.
4. Unscrew the base of the cyclone and place on a Kimwipe.
5. Grasp the cap of the housing and gently slide the unit from the housing onto the flat surface.
6. With a wrench disconnect the vacuum tube from the filter pack and set aside the cap and tube.
7. Record the serial numbers of the first, second, and third denuder tubes.

8. Disconnect the denuder tubes from the filter pack, coupling units, and cyclone, placing the tubes on a Kimwipe and the filter pack in the rack.
9. Check the sample ID number, the unit number, and the denuder tube numbers to make sure they correspond with those previously recorded.
10. Label the Teflon extraction vessels with the sample and filter ID's.
11. Unscrew the Teflon ring from the filter pack and remove the upper assembly.
12. Wearing plastic gloves and using clean forceps remove the filters, place them in the appropriately labelled containers and cap.

#### 1.12.2 Extraction of annular denuder tubes and filters.

Sampling tubes and filters, and the corresponding field and laboratory blank tubes and filters, should all be analyzed on the same day. Tubes and filters should be analyzed as soon after receipt of the sampling units from the field as possible. If immediate analysis is not possible, the ends of the tubes should be sealed with Parafilm, placed in a plastic bag, and stored in a covered, clean and dry container. Filters should be placed in the properly labelled petri dish, the dishes placed in covered container, and stored at 4°C.

#### 1.12.3 Filter Extraction

1. Using filter tweezers place the weighed filter into a 10 mL Teflon vial.
2. Pipette 20 mL of deionized water into each container (10 mL of water for nylon filters). Force the filter down in the container by inserting a piece of Teflon tubing split into three prongs.
3. Replace the cap on the container and place in a rack in the ultrasonic cleaning bath for one hour (at least ½ the container should be immersed).
4. Rinse the outside of the container with distilled water and dry with a Kimwipe.
5. Store the containers in a refrigerator at 4°C until analyzed (analyze as soon as possible).
6. After the sample extracts have been analyzed, the vials are rinsed eight times with deionized water and stored full of water prior to the next use.

#### 1.12.3 Denuder Extraction

1. Label the Teflon containers with the sample and tube ID's.

2. Place 5 mL of deionized water in the well of an extraction cap using an auto-pipetter (keep anion and ammonia tube extraction cups separate). Insert the tube in the cap and seal. Place a cap on the opposite end of the tube and seal. Rotate the tube to thoroughly wet all the surfaces with water. Let the extract drain to the bottom of the tube before opening the cap and pouring the liquid into the properly labelled Teflon container.
3. Repeat with a second 5 mL of deionized water and add to the first extract.
4. Replace the cap on the container and store at 4°C until analyzed (analyze as soon as possible).

### 1.13 Data Logger

The data logger will be interrogated weekly for the sampling period start and stop times and the 15 minute average flow rates.

### 1.14 Analytical Procedures

The analytical procedures are not covered in this protocol but are those of a competent analytical laboratory.

### 1.15 Calculations

The following calculations assume that sensitivity factors and any necessary corrections have been made in the chemical analysis to provide accurate concentration values.

#### 1.15.1 Concentrations of Gaseous Species (ug/m<sup>3</sup>)

##### 1.15.1.1 Nitric Acid (HNO<sub>3</sub>)

$$[\text{HNO}_3] = \{1016 \times ([\text{NO}_3^-]_{1\text{st}} - [\text{NO}_3^-]_{2\text{nd}}) \times V_{\text{ext}} / (F \times t)\}$$

where:

$[\text{NO}_3^-]_{1\text{st}}$  = concentration of NO<sub>3</sub><sup>-</sup> (ug/mL) in the extract from the first denuder tube

$[\text{NO}_3^-]_{2\text{nd}}$  = concentration of NO<sub>3</sub><sup>-</sup> (ug/mL) in the extract from the second denuder tube

$V_{\text{ext}}$  = extraction volume (mL).

$F$  = sampler air flow rate (L/min).



$t$  = sample time in minutes.

1016 = conversion factor for  $\mu\text{g}/\text{m}^3$

#### 1.15.1.2

Nitrous Acid (HONO)

$$[\text{HONO}] = \{(758 \times ([\text{NO}_2^-]_{1\text{st}} - [\text{NO}_2^-]_{2\text{nd}}) \times V_{\text{ext}} / (F \times t)\}$$

where:

$[\text{NO}_2^-]_{1\text{st}}$  = concentration of  $\text{NO}_2^-$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the first denuder tube

$[\text{NO}_2^-]_{2\text{nd}}$  = concentration of  $\text{NO}_2^-$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the second denuder tube

758 = conversion factor ( $\mu\text{g}/\text{m}^3$ )

#### 1.15.1.3

Sulphur Dioxide ( $\text{SO}_2$ )

$$[\text{SO}_2] = \{667 \times ([\text{SO}_4^{2-}]_{1\text{st}} - [\text{SO}_4^{2-}]_{2\text{nd}}) \times V_{\text{ext}} / (F \times t)\}$$

where:

$[\text{SO}_4^{2-}]_{1\text{st}}$  = concentration of  $\text{SO}_4^{2-}$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the first denuder tube

$[\text{SO}_4^{2-}]_{2\text{nd}}$  = concentration of  $\text{SO}_4^{2-}$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the second denuder tube

667 = conversion factor ( $\mu\text{g}/\text{m}^3$ )

#### 1.15.1.4

Ammonia ( $\text{NH}_3$ )

$$[\text{NH}_3] = \{944 \times [\text{NH}_4^+]_{3\text{rd}} \times V_{\text{ext}} / (F \times t)\}$$

where:

$[\text{NH}_4^+]_{3\text{rd}}$  = concentration of  $\text{NH}_4^+$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the third denuder tube

944 = conversion factor ( $\mu\text{g}/\text{m}^3$ )

### 1.15.2

Particulate Species

#### 1.15.2.1

Nitrate ( $\text{NO}_3^-$ ) ( $\mu\text{g}/\text{m}^3$ )

$$[\text{NO}_3^-] = \{1000 \times ([\text{NO}_3^-]_{\text{Te}} + [\text{NO}_3^-]_{\text{Ny}}) \times V_{\text{ext}} / (F \times t)\}$$

where:

$[\text{NO}_3^-]_{\text{Te}}$  = concentration of  $\text{NO}_3^-$  ( $\mu\text{g}/\text{mL}$ ) in the extract from the Teflon filter



$[\text{NO}_3^-]\text{Ny}$  = concentration of  $\text{NO}_3^-$  ( $\mu\text{g/mL}$ ) in the extract from the nylon filter

1000 = conversion factor ( $\mu\text{g}/\text{m}^3$ )

#### 1.15.2.2 Sulphate ( $\text{SO}_4^{2-}$ ) ( $\mu\text{g}/\text{m}^3$ )

$$[\text{SO}_4^{2-}] = \{1000 \times [\text{SO}_4^{2-}]\text{Te} \times V_{\text{ext}}/(F \times t)\}$$

where:

$[\text{SO}_4^{2-}]\text{Te}$  = concentration of  $\text{SO}_4^{2-}$  ( $\mu\text{g/mL}$ ) in the extract from the Teflon filter

1000 = conversion factor ( $\mu\text{g}/\text{m}^3$ )

#### 1.15.2.3 Ammonium ion ( $\text{NH}_4^+$ ) ( $\mu\text{g}/\text{m}^3$ )

$$[\text{NH}_4^+] = \{(1000 \times [\text{NH}_4^+]\text{Te}) + (290 \times [\text{NO}_3^-]\text{Ny})\} \{V_{\text{ext}}/(F \times t)\}$$

where:

$[\text{NH}_4^+]\text{Te}$  = concentration of  $\text{NH}_4^+$  ( $\mu\text{g/mL}$ ) in the extract from the Teflon filter

$[\text{NO}_3^-]\text{Ny}$  = concentration of  $\text{NO}_3^-$  ( $\mu\text{g/mL}$ ) in the extract from the nylon filter

NOTE: The  $\text{NH}_4^+$  concentration includes volatilized  $\text{NH}_4\text{NO}_3$  as calculated from the  $\text{NO}_3^-$  concentration on the nylon filter.

### 1.16 Data Reporting

#### 1.16.1 Laboratory Data

The following data is to be recorded for each sample set on a master data sheet in a laboratory notebook:

1. The unit ID and the serial numbers of the first, second, and third denuder tubes, together with the time and date when the unit was assembled.
2. The name of the laboratory analyst who prepared the unit.
3. The time and date when the unit is expected to start and stop sampling.
4. The time and date when the unit was shipped to the field, and the sampling location to which it was shipped.
5. The name of the shipper and the manifest number.

6. The time and date when a unit is received back in the laboratory, together with the unit number, the location from which it was shipped, and the name of the receiver.
7. The time and date the unit was disassembled and the filters and tubes extracted, the serial numbers of the tubes.
8. The concentrations ( $\mu\text{g/mL}$ ) of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_2^-$  in the extracts of the first and second denuder tubes, and the volume of the extract (10 mL).
9. The concentration ( $\mu\text{g/mL}$ ) of  $\text{NH}_4^+$  in the extract of the third denuder tube, and the volume of the extract (10 mL).
10. The concentration ( $\mu\text{g/mL}$ ) of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  in the extract from the Teflon filter, and the volume of the extract (10 mL).
11. The concentration ( $\mu\text{g/mL}$ ) of  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in the extract from the nylon filter, and the volume of the extract (10 mL). (The  $\text{SO}_4^{2-}$  analysis is not required but provides a check on possible contamination of the filter.)
12. The name of the analyst.

The data should be transferred to a computer program and stored on disc for use of the quality control officer.

#### 1.16.2 Field Log

The following data is to be recorded in the field log book and a copy shipped with each sampling unit to the laboratory:

1. Location, unit number, and date and time received.
2. Date and time installed.
3. Flow rate at the time of installation.
4. Date and time sampling period started and stopped.
5. Flow rate at the end of sampling period.
6. Notes about any flow calibration changes, leaks, or observations about the site or the sampling unit.
7. Date unit removed and shipped to the laboratory.
8. Name of the field operator.

The flow data will be transferred to the computer program and the field log sheet given to the quality control officer.

## 2 QUALITY ASSURANCE AND QUALITY CONTROL

The objective of the Quality Assurance plan is to provide, through well-defined QA functions, complete, precise, accurate, representative and comparable data. This objective is accomplished using a number of interrelated procedures. These procedures combine internal quality control (QC) of the measurement process and QA elements such as corrective action, data validation, and external assessment of precision and accuracy. The interplay of each of these functions ensure that the data generated are accurate and precise within well defined limits.

### 2.1 Quality Control Checks

#### 2.1.1 Denuder Blanks

Two extra sets of denuder tubes are coated along with the sampling tubes to be sent to the field. One set is retained in the laboratory and is used to detect any contamination in the coating solutions, in the tube cleaning and coating procedures, and in the extraction and analytical procedures.

#### 2.1.2 Field Blanks

The second set is assembled into a sampling unit and shipped to the sampling location. It is mounted on the trolley and attached to the vacuum line but the valve to the line is closed and there is no flow through the unit. At the end of a normal sampling period the unit is capped and shipped back to the laboratory. This permits any contamination due to assembly, shipping and installation to be detected.

#### 2.1.3 Flow Checks

Beginning and end flow should agree within 10 percent. If not, the sample should be flagged.

#### 2.1.4 Sampling Period Checks

The sampling date and period from the data logger should agree with that of the laboratory log. The period with flow, as recorded from the mass flow controller, should correspond with the sampling period programmed into the data logger.

#### 2.1.5 Unit Checks

The unit number and denuder tube serial numbers recorded in the laboratory log book and the field log book at the times of assembly, shipping, installation, and disassembly should correspond.

### 2.1.6 Flow Calibration

The mass flow controller and the flow meter used in the field should be checked against a primary standard (such as a bubble meter) every 6 months. Any discrepancies greater than 2 percent should be noted and brought to the attention of the quality control officer.

### 2.1.7 Repipet Calibration

Repipet calibration is done prior to the extraction of each set of filters. Pipet 10 mL of solution into a 10 mL volumetric flask. If required adjust pipet until it delivers within 2 mm of the 10 mL mark. This represents an error of less than 1%. Three successive deliveries should be within 2% of each other. Three vials will be filled with the extraction solution, either deionized water or IC eluent. The vials will then be treated and analyzed as samples. These "blank" analytical results will be recorded and a running plot of the data maintained.

## 2.2 Quality Controls

A single quality control officer should be responsible for overall quality control. This officer should receive copies of all notes and data from the field log, the laboratory notebook, and the data logger so that unusual ambient air concentrations can be examined and compared to field and laboratory activities. Any difficulties encountered either in the field or in the laboratory should be reported to this person. QC procedures for the chemical analysis are performed in the laboratory and are not reported in detail here. They consist of the use of calibration curves, standard solutions, laboratory and field blanks, duplicates, and spiked samples. (See appendices).

### 2.2.1 Analytical Laboratory Log

An example of an Analytical Laboratory Log is shown in Figure 7.

## 2.3 Corrective Action

Corrective actions should be performed as shown in Table 2.

## 2.4 Method Precision and Accuracy

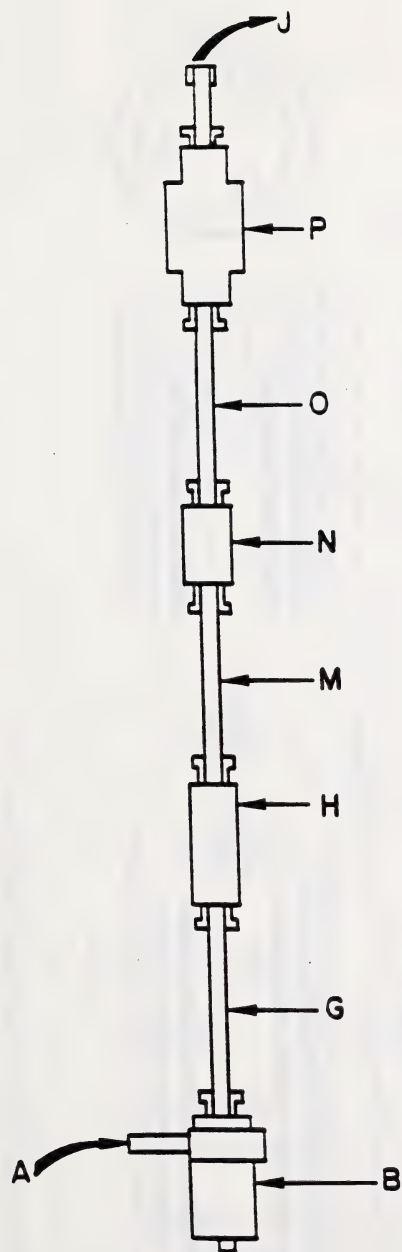
Initial field tests indicate a precision of +7% or +0.07  $\mu\text{g}/\text{m}^3$ , based on a 24 h sampling period at a flow rate of 7.1 Lpm. The limits of detection are  $<0.1 \mu\text{g}/\text{m}^3$  for  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . The detection limit for  $\text{NH}_3$  is  $<0.2 \mu\text{g}/\text{m}^3$ .



Table 2. Quality Control Corrective Actions

Condition	Action
Note that when temperatures went down near the $-30^{\circ}\text{C}$ range, the lines to the denuder system were very brittle and broke when moved even slightly and the connector between the denuder caps and the vacuum lines would not seal. The vacuum lines had to be disconnected and warmed inside the trailer. Also, at these temperatures, methanol had to be used in the capmon ports to get the quick couple connectors to properly connect to the filter packs.	Tubing design changed.
Flow at vacuum line does not agree with mass flow controller setting.	Note problem in log book. Check for kinks in the line. Check for leaks. Check calibration of mass flow controller and adjust. Note flow adjustment in log.
Flow at inlet does not agree with mass flow controller setting.	Note problem in log book. Check assembly of pieces. Check seating of parts and tighten fittings.
Beginning and end of sampling period flow rates do not agree within $\pm 10\%$ .	Note problem in field log. Check mass flow calibration. Filters may be clogged, check flow at end of vacuum line. Check vacuum line for kinks. Check for leaks. Note any corrective action.
Contaminated laboratory blank.	Note problem in laboratory book. Pay close attention to the parts cleaning procedure. Analyze deionized water.
Contaminated field blank.	Note problem in laboratory book. Pay close attention to parts assembly procedure. Ensure the units are properly capped during shipping.





## LIST OF COMPONENTS

- A. Inlet
- B. Cyclone
- G. First denuder tube,  $\text{Na}_2\text{CO}_3$
- H. Coupling unit
- M. Second denuder tube,  $\text{Na}_2\text{CO}_3$
- N. Coupling unit
- O. Third denuder tube, citric acid
- P. Filter pack
- J. Outlet

Figure 1. Annular Denuder - Filter Pack System

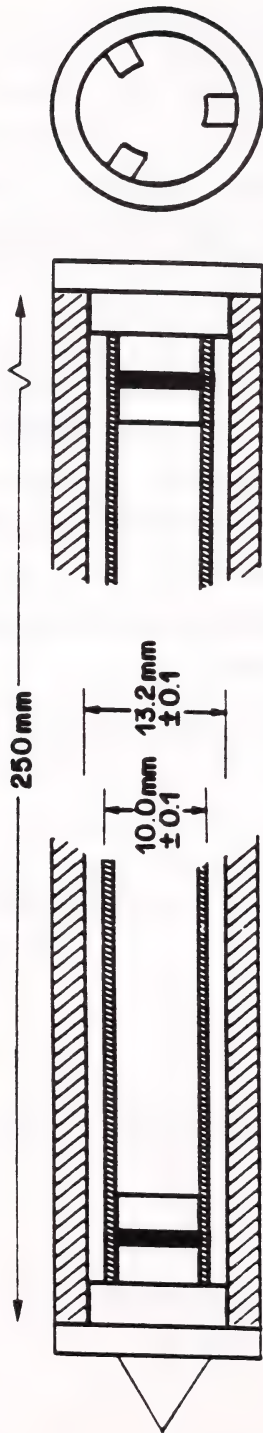


Figure 2a. Design of the First and Third Annular Denuder Tubes (G,O)

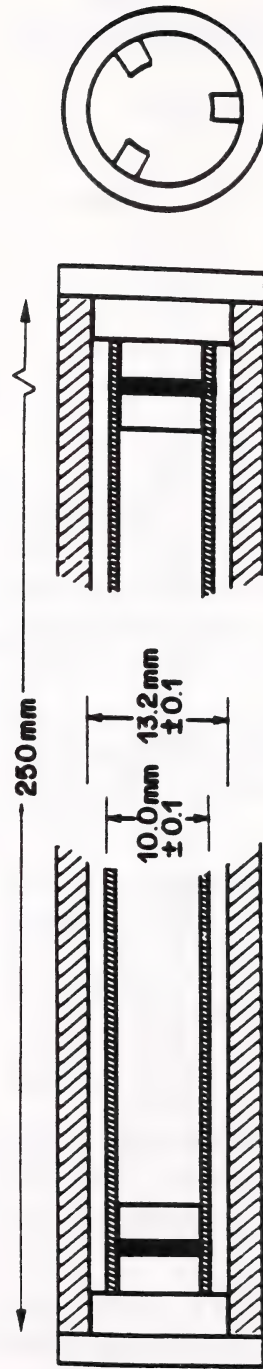


Figure 2b. Design of the Second Annular Denuder Tube (M)

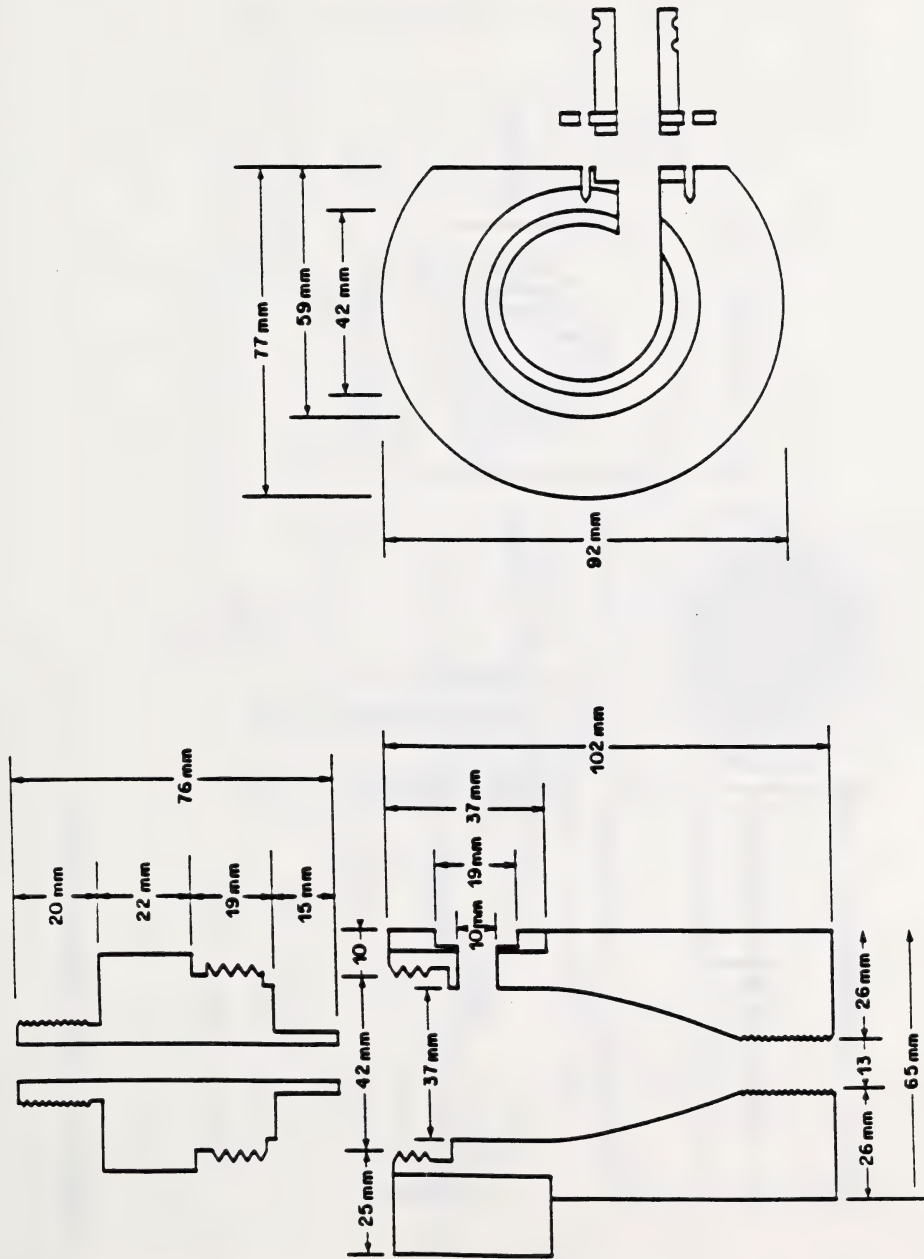


Figure 3. Design of the Teflon Cyclone (B). (Dimensions may vary according to sampling volume requirements.)

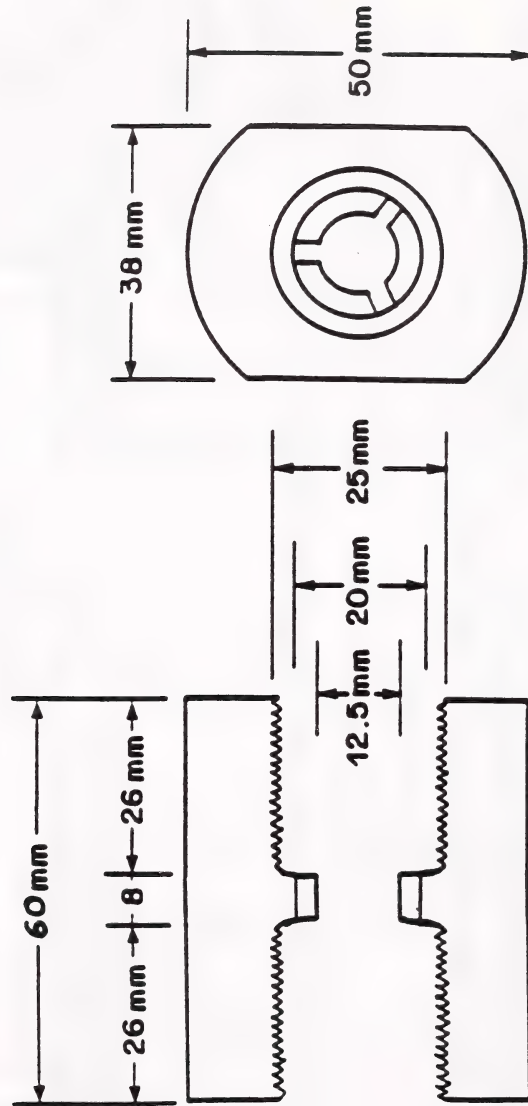


Figure 4. Design of the Tube Connector, (H, N)

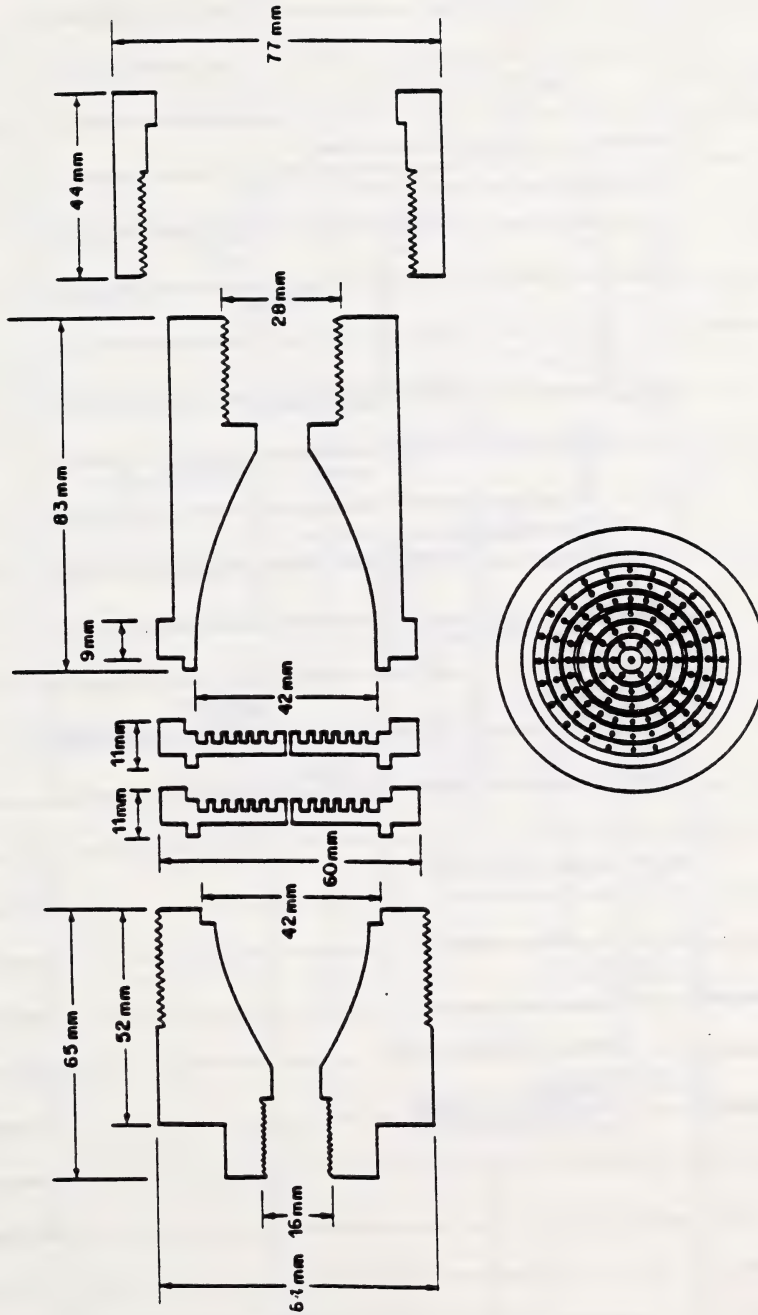


Figure 5. Design of the Filter Pack (P)



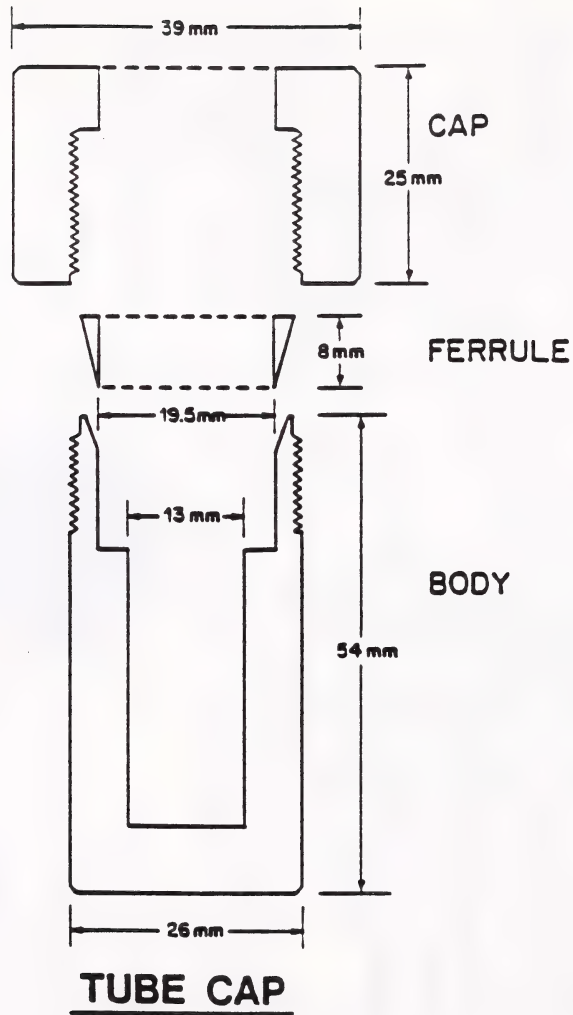


Figure 6. Dimensions of Tube Extraction and Coating Cap

BOOK NUMBER ADS	SITE		SAMPLE NUMBER	AD6-P
Date Prepared				BLANK:
				(Month:Day:Year)
Sampling Period		(1 or 6 days, or blank)	Flow Rate	
				(Lpm)
Designated Start Time			(Hour:Minute)	
Designated Start Date				(Month:Day:Year)
Designated Stop Time			(Hour:Minute)	
Designated Stop Date				(Month:Day:Year)
Actual Start Time			(Hour:Minute)	
Actual Start Date				(Month:Day:Year)
Actual Stop Time			(Hour:Minute)	
Actual Stop Date				(Month:Day:Year)
T1#			Teflon filter sample weight	
T2#			Final Weight	
T3#			Initial Weight	
FP#	AD6-			
COMMENTS				

2440-DN3-1/1

121000014.FRM/BF/uah/92/04/29

## APPENDIX A

### PROCEDURE FOR THE ANALYSIS OF MAJOR IONS BY ION CHROMATOGRAPHY





## APPENDIX A

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## 1 INTRODUCTION

Ion chromatography is a technique which employs ion exchange, eluent suppression, and conductometric detection to quantify levels of strong acid anions such as sulphate, nitrate and chloride. In the Dionex model 2020i chromatograph, a low-capacity separator column provides high efficiency separation of anions through competition of the anions and the eluent for active sites on the column. The degree of species separation and retention time depends on the relative affinities of different ions for the active sites, eluent strength and eluent flow rate. An eluent containing  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  has been found to be particularly effective in the resolution of sulphate and nitrate ions, as well as other ions commonly found in aerosol filter samples and rainwater. After separation, the eluent plus sample stream passes through a suppressor column which converts the eluent from a high conductivity form to a low conductivity form ( $\text{H}_2\text{CO}_3$  in this case). The suppressor column is continuously regenerated. The anions of strong acids remain dissociated and are detected by means of their electrical conductivity.

For comparability to other components generally found in aerosol filter samples, the results of analyses are reported in terms of nanoequivalents of ionic species per millilitre. Precision of analyses is approximately 10% for samples above 20neq/mL. Below this limit, variations are approximately 0.2neq/mL.

When several ions are being measured at the same time (for example, sulphate and nitrate), the procedures described herein are understood to apply to both of the ions. (i.e., if a quality control result for sulphate is satisfactory but the nitrate is not, initiate action as if both were out-of-control).

## 2 EQUIPMENT

### 2.1 Ion Chromatograph

The major components of the commercial instruments are listed below.

2.1.1 Precolumn - 3x150 mm anion column which serves to guard the separator column from reactive ions and particulate matter.

2.1.2 Separator column - 3x500 mm anion column containing the resin on which the ion separation takes place.

2.1.3            Anions Self-Regenerating Suppressor - A cartridge containing a node and cathode electrodes separated by ion exchange membranes. Water flowing through the unit is electrolytically hydrolyzed supplying regenerated hydronium ions. In a micromembrane suppressor, a flow of chemical reagent supplies hydroxide ions for a neutralization reaction.

2.1.4            Conductivity cell - A 1.5 microlitre volume cell in which the electrical conductivity of the eluent stream is measured.

2.1.5            Pumps - Dual-piston constant pressure/constant flow pumps are used to pump the required liquids at pressures up to about 1800 psi. Flow rates are linearly variable from 0.1 to 9.9mL/min in 0.1mL/min increments.

2.1.6            Valve system - A complex array of air-actuated valves controls the liquid flows through the system. Valves and columns are interconnected with Teflon tubing (1/32inch i.d. by 1/16" o.d.)

## 2.2            Compressed Air System

A continuous supply of 80 psi compressed air is required for valve actuation. Either a house air supply or compressed air cylinders with regulators may be used.

## 2.3            Deionized Water System (DI Water System)

Required for reagent preparation and rinse cycles in column regeneration. A Barnstead glass still with a Nanopure four cartridge system and 0.45µm final filter produces HPLC grade water.

## 2.4            General Supplies

2.4.1            3 cc disposable syringes for manual loading of samples (Becton Dickenson #5585).

2.4.2            Disposable 5.0 or 0.5 mL vials and filter caps for loading of samples in the automatic mode.

2.4.3            10 litre polyethylene carboys with spigots for storage of eluent.

2.4.4            10 litre polyethylene carboys capable of being pressurized for storage of regenerant.

## 2.5            Auto Sampler

A Dionex autosampler may be used for automatic loading of samples.

## 2.6 Manuals

Operating manuals for the following components:

- 2.6.1 Dionex ion chromatograph.
- 2.6.2 Dual-piston constant pressure/constant flow pump.
- 2.6.3 Autoion 100 controller.
- 2.6.4 Dionex automated sampler.
- 2.6.5 Hewlett Packard 3390A integrator.

## 2.7 Logbook

The logbook contains quality control charts, data concerning blanks, and maintenance information.

## 3 REAGENT PREPARATION

All prepared solutions are to be labelled with the preparation date, operator's initials, and contents.

### 3.1 Stock Solutions for Standards

ACS certified reagent grade chemicals are oven-dried at 105°C for one half hour and cooled prior to weighing. New stock standards are prepared yearly. An exception is the  $\text{SO}_3^-$  standard which must be prepared monthly.

#### 3.1.1 Stock $\text{Cl}^-$ 1000 ppm

Weigh 1.6484 g NaCl and transfer to a 1000mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

#### 3.1.2 Stock $\text{NO}_2^-$ 1000 ppm

Weigh 1.4998 g  $\text{NaNO}_2$  and transfer to a 1000mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

#### 3.1.3 Stock $\text{NO}_3^-$ 1000 ppm

Weigh 1.3707 g  $\text{NaNO}_3$  and transfer to a 1000 mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

#### 3.1.4 Stock $\text{SO}_4^{=}$ 1000 ppm



Weigh 1.4780 g  $\text{Na}_2\text{SO}_4$  and transfer to a 1000mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

3.1.5 Stock  $\text{SO}_3^-$  100 ppm in 0.1% Formaldehyde.

Weigh 0.1575 g  $\text{Na}_2\text{SO}_3$  and transfer to a 1000mL volumetric flask. Dissolve in 900 mL DI  $\text{H}_2\text{O}$  with 1mL formaldehyde. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.1.6 Stock  $\text{PO}_4^-$  1000 ppm

Weigh 1.2112 g  $\text{NH}_4\text{H}_2\text{PO}_4$  and transfer to a 1000mL volumetric flask. Dilute to mark with DI  $\text{H}_2\text{O}$ .

### 3.2 Intermediate Stock Standards

These solutions are prepared monthly.

3.2.1 Intermediate Stock A

10 ppm  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$  combined.

Pipette 10.0 mL each of 1000 ppm  $\text{Cl}^-$ , 1000 ppm  $\text{NO}_3^-$ , and 1000 ppm  $\text{SO}_4^-$  stock solution into a 1000mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

3.2.2 Intermediate Stock B, 10 ppm  $\text{NO}_2^-$

Pipette 10.0 mL of 1000 ppm  $\text{NO}_2^-$  stock solution into a 1000mL volumetric flask.

Dilute to the mark with DI  $\text{H}_2\text{O}$ .

3.2.3 Intermediate Stock C, 10 ppm  $\text{PO}_4^-$

Pipette 10.0 mLs of 1000 ppm  $\text{PO}_4^-$  stock solution into a 1000 mL volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

### 3.3 Working Standards

3.3.1 Working Standard Solutions

These solutions are prepared daily.

3.3.1.1 3000 ppb  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$

Pipette 30.0 mL of intermediate stock A into a 100mL volumetric flask. Add 10 mL concentrated eluent (see Section 3.4). Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.2 1000 ppb  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$

Pipette 10.0 mL of intermediate stock A into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.3 500 ppb  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{=}$ 

Pipette 5.0 mL of intermediate stock A into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.4 200 ppb  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{=}$ 

Pipette 2.0 mL of intermediate stock A into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.5 100 ppb  $\text{NO}_2^-$ 

Pipette 1.0 mL of intermediate stock B into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.6 100 ppb  $\text{PO}_4^{=}$ 

Pipette 1.0 mL of intermediate stock C into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.3.1.7 500 ppb  $\text{SO}_3^{=}$ 

Pipette 0.5 mL of 100 ppm  $\text{SO}_3^{=}$  stock into a 100mL volumetric flask. Add 10 mL concentrated eluent. Dilute to mark with DI  $\text{H}_2\text{O}$ .

3.4 Preparation of Eluent and Regenerant Solutions3.4.1 Concentrated eluent (1.7 mM  $\text{NaHCO}_3$  and 1.8 mM  $\text{Na}_2\text{CO}_3$ )

Weigh  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  and transfer to a 2L volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ .

## 3.4.2 Working eluent (made daily)

With a graduated cylinder, transfer 100 mL concentrated eluent solution to a 1L volumetric flask. Dilute to the mark with DI  $\text{H}_2\text{O}$ . Transfer to eluent carboy. Volume of concentrated eluent used is dependent upon the column, the retention time, and degree of separation required. Transfer to eluent carboy.

3.4.3 Regenerant Solution 0.025 M  $\text{H}_2\text{SO}_4$  (made daily)

Add 2.8 mL concentrated  $\text{H}_2\text{SO}_4$  (36N, 18M) to 4L of DI  $\text{H}_2\text{O}$ . Transfer to regenerant carboy.

## 4 ANALYTICAL PROCEDURES

### 4.1 Startup Procedure for Analytical Pump

- 4.1.1 Ascertain that there are sufficient levels of eluent and regenerant. Refill if necessary.
- 4.1.2 Turn on compressed gas (air or nitrogen) to 110psi.
- 4.1.3 Turn on eluent spigot at carboy.
- 4.1.4 Set regenerant pressure to 15 psi.
- 4.1.5 Press the appropriate eluent valve number on the analytical pump.
- 4.1.6 Connect an empty 10 mL syringe to the Luer adaptor on the priming valve.
- 4.1.7 Turn the small handle on the priming valve to align with the syringe.
- 4.1.8 Slowly draw out liquid into the syringe. Repeat twice.
- 4.1.9 Turn small handle on priming valve to align with pump face.
- 4.1.10 Set the flow to 2.0 mL/min.
- 4.1.11 Set the Stop/Start switch to start. The column pressure will increase to 1000-1400 psi (depending upon the column in use); when the pressure is stabilized the ready light will come on.
- 4.1.12 Set the pressure limit select to the following values:
  - LOW - 50 x 10 psi
  - HIGH - 17 x 100 psi.
- 4.1.13 Local/Remote switch - set to Remote.

### 4.2 Start Up Procedure for Analytical Module

- 4.2.1 Set Local/Remote switch to Remote.
  - 4.2.2 Set temperature compensation to 1.7.
  - 4.2.3 Select the proper operating range for the detector, usually 1 ms.
  - 4.2.4 When ready light comes on, set cell On/Off to ON.
  - 4.2.5 When conductivity remains stable and below 30ms, set Auto offset On/Off to ON.
- The detector readout of the conductivity has reset the baseline to zero.

### 4.3 Computer is Programmed for Various Methods and Parameters

- 4.3.1 Select the following parameters:
- 4.3.2 These parameters may be changed to accommodate the system conditions at analysis time. Note: Parameters must be re-entered after a power shut-down.

#### 4.4 Startup Procedure for Advanced Chromatography Module

- 4.4.1 Set Load/Inject Switch to LOAD.
- 4.4.2 Rinse sample loop with 2 mL of DI H<sub>2</sub>O.
- 4.4.3 Valve A OFF
- 4.4.4 Valve B OFF
- 4.4.5 Local/Remote switch set at LOCAL.

#### 4.5 Analysis

4.5.1 Using a 3 mL disposable syringe, load an eluent sample into the Luer adaptor of the sample port. All samples and standards must be spiked with eluent to prevent the occurrence of a water dip on the chromatogram. The eluent peak may be eliminated by matching the concentration of the eluent in the sample to the concentration of the eluent in the working eluent solution (Section 3.4.2). Samples and standards may be made up in or extracted with eluent solution or may be spiked with concentrated eluent before analysis.

- 4.5.2 Start integrator.
- 4.5.3 Press Load/Inject switch to INJECT.
- 4.5.4 High quality water and uncontaminated eluent produces only an eluent peak.
- 4.5.5 When the system conductivity has returned to 0ms (it may be necessary to Autozero the background conductivity between samples), set the Load/Inject switch back to LOAD.
- 4.5.6 Load and inject samples and standards as above.

#### 4.6 Shutdown

- 4.6.1 Turn the Auto offset switch to "OFF".
- 4.6.2 Turn the Detector cell to "OFF."
- 4.6.3 Turn pump OFF.
- 4.6.4 Wait for READY light to go off.



- 4.6.5 Turn selected eluent valve OFF.
- 4.6.6 Turn off spigot valve to eluent carboy.
- 4.6.7 Release pressure from regenerate pressure regulator.

## 5 CALCULATIONS

### 5.1 Sample Analysis by Area Measurement

The Hewlett-Packard Integrator calculates the area under specified peaks. Unknown concentrations are determined by comparing the peak area to that of a standard.

5.1.1 Calculate the slope for each ion by linear regression using the area values determined by the standards.

5.1.2 Sample ion concentration = sample area x slope.

5.1.2.1 Note that the slope is a function of how the sample was spiked with eluent in comparison to how the standard was spiked with eluent. If a sample concentration is diluted by the addition of eluent, then the slope must be adjusted accordingly.

## 6 DATA STORAGE AND REVIEW

### 6.1 Chart Recordings

Strip chart recordings (Hewlett-Packard Integrator Output) are dated and retained in the laboratory for a period of at least two years.

### 6.2 Data Records

The determined concentrations of the samples are entered manually into file on the laboratory computer system. Files are identified by a file name which is a combination of the site, date, and month. An example is VEGR 1286.KAP. A hard copy listing of this data is automatically generated. This listing is delivered to the Laboratory Supervisor for review. The data listing then becomes a section of the monthly report.



### 6.3 Data Review

All results are examined before being released from the laboratory. The data listing must be initialled and dated. Any suspected irregularities should be examined; if need be, repeat analyses on a selected group of samples may be called for. Particular attention is paid to the results from the calibration and quality control samples.

## 7 QUALITY CONTROL

At a minimum every seventh sample in a series of analyses is a quality control. Quality controls include standards, blanks, and replicates. Quality control charts are prepared from the results of the quality control standards.

### 7.1 Quality Control Standards and Control Charts

7.1.1 At least one quality control sample shall be analyzed each day of analysis. Several levels of concentration for quality control standards are provided in order to best match the range of concentration of the unknown samples.

7.1.2 Quality Control Charts are prepared as soon as possible after analysis in order to rapidly detect operating abnormalities. Current outer control limits are + 10% for QC solutions. Excursions past the control limits require the actions described in Section 10.

### 7.2 Blanks

In-house blanks are samples of extracting solution which are bottled and treated in the same way as the regular unknowns. This type of blank pinpoints problems such as contamination in extracting bottles, extracting solution or deionized water. Values for these blanks are recorded in the instrument log book. The analysis of filter blanks is generally of importance in aerosol studies.

## 8 MAINTENANCE

A schedule of maintenance is listed in Table 1.

Table 1. Maintenance Schedule

<u>Action</u>	<u>Schedule</u>
Oil pumps	Every 2 months
Clean conductivity cell	Every 2 months
Replace separator column	Approximately annually depending on use and pressure buildup.
Replace suppressor column	Approximately annually, depending on use.
Replace guard column	Approximately annually, depending on nature of samples.
Reflare Teflon tubing	Whenever leaks appear.

## 9 QUALITY ASSURANCE

### 9.1 Traceability of Standards

Standards are prepared from dried ACS certified materials.

## 10 CORRECTIVE ACTION

All out-of control situations are to be reported to the Laboratory Supervisor and recorded in the instrument logbook which is maintained in the laboratory. All corrective actions are to be similarly reported. Table 2 presents a list of out-of-control situations and the corresponding corrective action.

Table 2. Analytical problems and solutions

<u>Conditions</u>	<u>Actions</u>
Two initial standards differ by more than 5%.	Repeat standards until instrument stabilizes.
Quality control standards differ by more than 10%.	Determine source of problem and rerun all samples since last acceptable QC result.

## 11 QUALITY ASSURANCE REPORTS

11.1 Quality Assurance activities will be discussed in the weekly reports prepared by the operator for the laboratory supervisor. In particular, any out-of-control situations should be described along with the corrective actions.

Quality Assurance Activities: (Include information on any out-of-control situations and corrective actions; list date of performance audits; describe major maintenance).

## 12 TROUBLESHOOTING

The following solutions are meant as a guide to commonly occurring problems. Detailed procedures are found in the Dionex manual.

### 12.1 Pump Problems

Symptoms are loss of pump prime, pump will not start, pump stops, ready LED does not light, eluent manifold leaks or pump leaks.

- 12.1.1 Inspect tubing for air.
- 12.1.2 Prime pump with methanol.
- 12.1.3 De-gas eluent.
- 12.1.4 Check piston seal.
- 12.1.5 Check piston movement.
- 12.1.6 Check valve.

12.2        Suppressor Problems

Symptoms are drifting base line and loss of suppression.

12.2.1       Check regenerant flow - should be at least 20% greater than eluent flow.

12.2.2       Check to see if eluent is going through suppressor outlet.

12.2.3       Remake eluent and regenerant solution.

12.2.4       Check suppressor fittings.

12.3        Column Problems

Symptoms are loss of resolution, loss of retention, missing peaks, abnormal operating pressures, unusual colours, abnormal peak shape, or large column voids.

12.3.1       Replace bed supports in guard column.

12.3.2       Replace bed supports in column.

12.3.3       Clean guard column.

12.3.4       Clean column.

12.3.5       Replace the column.

12.4        Problems With Conductivity Detector

Symptoms are noisy or drifting baseline.

12.4.1       Check for flow system leak ahead of the cell.

12.4.2       Allow for longer system equilibrium.

12.4.3       Check for air trapped in cell.

## APPENDIX B

### PROCEDURES FOR THE EQUILIBRATION AND WEIGHING OF MEMBRANE FILTERS





## APPENDIX B

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## 1 INTRODUCTION

Described are the procedures for the equilibration of the Teflon membrane filters at constant temperature and humidity, the gravimetric determination of the mass of the aerosols collected, and the extraction of the filters prior to chemical analysis.

## 2 EQUIPMENT

Electronic microbalance Mettler M3, or equivalent: This balance has built in taring weights with NBS Class M accuracy and has a weighing range of 0-150 mg. The manufacturer's specification sheet and manual are included in this appendix.

Temperature and humidity controlled cabinet: A glove box, approximately 20" X 20" X 36", modified to provide temperature control at 30°C and 50 % relative humidity is required to allow weighings to be made without disturbing the temperature or humidity.

Filter weighing pan: It replaces normal balance weighing pan and is designed to accommodate filters up to 50 mm in diameter.

Epoxy balance table: Used to provide a stable, vibration free, support for the balance.

Po 210 source: Neutralizes electrostatic charges on the filters. (Note: a AEC license is required to purchase this radioactive source)

Two sets of filter tweezers: For handling the membrane filters.

Petri dishes of greater than 50mm in diameter: Used for equilibration and storage of filters.

### 2.1 Equipment Installation

1. The balance table is set up in a clean laboratory, preferably in a biological clean room.
2. The balance is set on the table, levelled and calibrated according to the manufacturers instructions.
3. The humidity cabinet is placed over the balance and sealed to the surface of the balance table.
4. Place the Po 210 source in the balance weighing chamber.

5. Adjust the humidity and temperature controls to equilibrate the cabinet and the balance at 30°C and 50 % relative humidity.

### 3 PROCEDURE

#### 3.1 Equilibration and Weighing of New Filters

1. Because the membrane filters to be weighed cannot be labelled directly, label the petri dishes with the sample number (notebook number, notebook page, and filter number).
2. Label a petri dish for the "standard filter".
3. Using the filter tweezers place a Teflon membrane filter in each dish. (Make sure the paper filter divider is not picked up with the filter.)
4. Place the open petri dishes containing the filters in the humidity cabinet, arranging them in order of their sample number for ease of weighing.
5. Allow the filters to equilibrate under constant temperature and humidity for at least two hours.
6. Ensure that the humidity and temperature in the cabinet are within the specified range.
7. Do not open the cabinet. Use the gloves for the following procedures.
8. Zero and calibrate the balance as per the procedures in the manufacturer's operating manual.
9. All weighings are made in the 100 mg weighing range.
10. Using the tweezers to move the filters from the petri dishes to the balance pan, weigh the standard filter and the other filters and return them to their correct petri dishes.
11. Record the weight of the standard filter, and the filters to be used for sampling, on the appropriate pages of the notebook.
12. Re-weigh the standard filter between every fourth filter weighing. These replicate weighings should not vary by more than 0.005 mg.
13. Check the calibration of the balance after every 25 weighings and at the end of each set of weighings. It should not differ by more than 0.005 mg.



14. Should the weight of the standard filter change by more than 0.005 mg, check the humidity and temperature in the chamber and allow the filters to equilibrate at least a further two hours before re-weighing.
15. Remove the petri dishes with sampling filters from the humidity cabinet.
16. The filters are now ready to be loaded into the filter packs. Retain the numbered petri dishes for use when the filters are returned after sampling.

### 3.2 Equilibration and Weighing of Filters After Sampling

1. Ensure that the filter after sampling is returned to the correctly labelled petri dish and place the open dish in the humidity cabinet.
2. Note any damaged filters, or non-uniform distribution of particles on the filter, in the laboratory notebook and report to the laboratory supervisor.
3. Follow the previously described procedures for equilibrating and weighing filters (Section 3.1).
4. Report any anomalous filter weights to the laboratory supervisor.

## 4

### CALCULATIONS

The following calculations are performed after weighing the sampled filters:

1. Calculation of the mass of aerosol deposited

$$(M_s - M_f) - (M_a - M_f) = M_a$$

where  $M_s$  = mass of filter after sampling in mg

$M_f$  = mass of standard filter in mg

$M_a$  = mass of filter prior to sampling in mg

$M_a$  = Mass of aerosol collected in mg.

2. Calculation of mass per unit volume of air sampled

$$M_v = \frac{M_a}{F \times t}$$

where  $M_v$  = mass per unit volume in  $\mu\text{g}/\text{m}^3$

$F$  = sampling rate in litres per minute

$t$  = duration of sampling period in minutes

## QUALITY CONTROL AND QUALITY ASSURANCE

## 5.1

Quality Control

The steps taken to control the quality of mass determined gravimetrically are summarized as follows:

1. Weighing room and environmental chamber conditions are kept within specified bounds and documented.
2. Balance zero must not drift from the beginning to the end of a weighing session by more than  $\pm 0.005$  mg.
3. Replicate weighings of standard filters must agree within  $\pm 0.005$  mg for a given weighing session and to within  $\pm 0.001$  mg for the weighings of the standard filter during the initial filter weighing and the weighing after the sample is collected.
4. "Negative" mass of collected aerosol. A negative sample weight may (but not always) result from filters being returned to the wrong petri dish. This requires prompt assessment of the situation to avoid invalidation of the data from the entire sampling set.

## 5.2

Quality Assurance

## 5.2.1

## Precision and detection limit

The precision of the mass of aerosol deposited is a function of the precision of the weighing of the filters and in the precision in maintaining constant temperature and humidity.

The precision in weighing the filters can be determined as follows:

1. Equilibrate and weigh 72 Teflon filters and mount in the filter packs.
2. Seal the filter packs and attach to the sampling unit but do not turn on the sampling pump.
3. Remove the filters from the filter packs, inspect for any damage, equilibrate, and weigh.

4. Calculate the mean "deposited mass" and the standard deviation of the deposited mass using:

$$\text{mean } M_a = (\text{sum } M_{a1} + M_{a2} + \dots + M_{a72})/72$$

$$\text{Std dev } M_a = [(\text{sum } M_{a1}^2 + M_{a2}^2 + \dots + M_{a72}^2)(1/71) -$$

$$(\text{sum } M_{a1} + M_{a2} + \dots + M_{a72})^2(1/5112)]^{1/2}$$

The precision is considered to be one standard deviation and the detection limit to be 4.65 times the standard deviation.

#### 5.2.2 Accuracy

The accuracy of the balance is established through the use of built-in weights. The accuracy of these weights is as follows:

Mechanical weights - 1000 mg range  $\pm 20 \text{ ug}$

- 100 mg range  $\pm 10 \text{ ug}$

Electrical weights - 100 mg range  $\pm 1 \text{ ug}$

#### 5.2.3 Data review

All data must be reviewed by the laboratory supervisor and the quality control officer.

### 5.3 Corrective Action

Corrective actions for failure of the balance are described in detail in the balance operating manual.

Failures must be reported to the laboratory supervisor and service by the manufacturer may be required.



## APPENDIX C

### ALBERTA ENVIRONMENTAL PROTECTION PRECIPITATION QUALITY MONITORING SITE SELECTION CRITERIA





<u>Criteria</u>	<u>Reason</u>
1. Height above ground, 1-3 m	1. To reduce or eliminate the influence of ground level absorbing surfaces such as grass and other foliage.
2. Elevation angle to top of any obstruction, <30 degrees.	2. To reduce or eliminate the influence of turbulence.
3. Distance from major stationary fuel combustion or industrial source (greater than 25 tonnes/ day SO <sub>2</sub> or NO <sub>x</sub> ), >30 km.	3. To prevent non-representative effects on regional precipitation quality.
4. Distance from dust source (ie. roads), >100 m.	4. To reduce or eliminate the influence of dust on precipitation quality.
5. Distance from AC power source no greater than 100 m.	5. To prevent significant loss of voltage in power cord.
6. Instrument orientation, an East-West direction.	6. To allow deposition into the bucket without undue influence of turbulence caused by the physical presence of the instrument.
7. Site security; within areas that allow restricted access or no access by the public.	7. To prevent tampering and vandalism by unauthorized personnel.
8. Co-location with standard rain gauge.	8. To provide actual precipitation data since the Sangamo loses some due to evaporation.
9. Flat and grassy terrain.	9. To reduce or eliminate the influence of local dust source on precipitation quality.

Note that the ultimate choice for each site will be a compromise optimizing these various criteria.

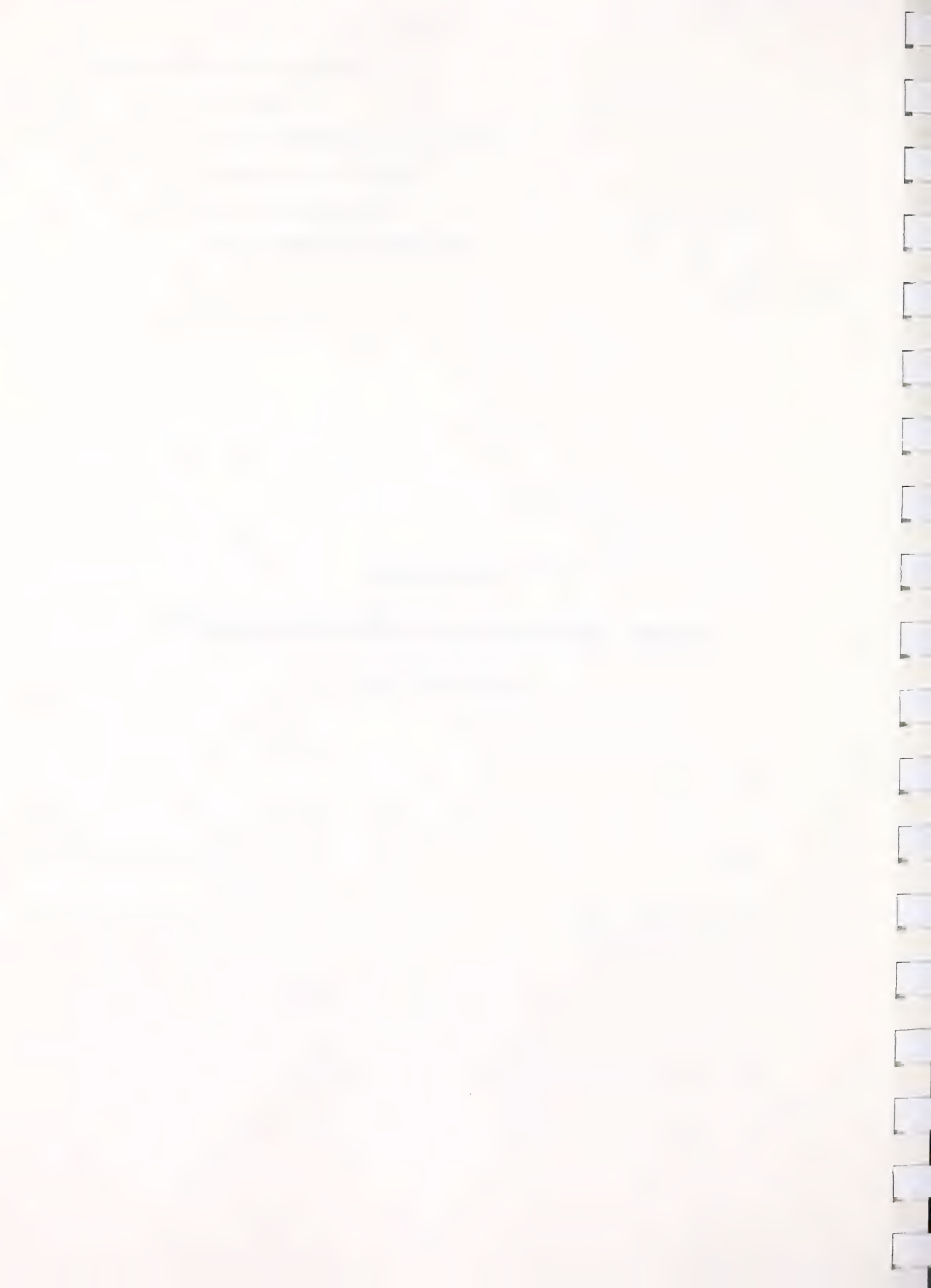
Record unusual site occurrences:

- dust in air
- cultivation/spraying/fertilizing near site
- construction at or near site
- snow ploughing at site
- smoke/odour/ash detected at site.

APPENDIX D

ANIONS, DISSOLVED (ION CHROMATOGRAPHY)

METHOD 52121





## ANIONS, DISSOLVED

(Ion Chromatography)

### 1. Introduction

- 1.1 Ion chromatography is particularly well suited for the analysis of anions in precipitation samples. In particular, sulphate is detectable at lower concentrations than by other methods. The anions  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  are analyzed simultaneously in an eight-minute run.

### 2. Principle

- 2.1 Like other chromatographic techniques, ion chromatography consists of a stationary phase (the ion exchange resin) and a mobile phase (the eluent). The equilibrium of the ion between the two phases governs the amount of time that the ion is retained in the column. Those ions with the least affinity for the exchange site are carried through first by the eluent stream.
- 2.2 The technique consists of injecting the sample by means of a sample loop into the eluent stream. The eluent carries it sequentially through the separator column, the micro membrane suppressor and the conductivity detector. The eluent for anions is dilute carbonate-bicarbonate solution (0.0020 M  $\text{Na}_2\text{CO}_3$ /0.0025 M  $\text{NaHCO}_3$ ). The separator is a pellicular anion-exchange resin and has affinity for anions in the following order:  $\text{F}^- < \text{CO}_3^{2-}, \text{HCO}_3^- < \text{Cl}^- < \text{NO}_2^- < \text{Br}^- < \text{NO}_3^- < \text{PO}_4^{3-} < \text{SO}_4^{2-}$ . When the eluent carries the sample through the separator, the ions with greater affinity are retained longer in the column. They leave the separator as their sodium salts and then enter the micro membrane suppressor.
- 2.3 The suppressor removes the background conductivity arising from the eluent. It does this by exchanging all the cations for hydrogen ion. This converts the highly conducting  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  to  $\text{H}_2\text{CO}_3$ , which has a very low conductivity. It also converts all the anions of interest to their acid form (i.e.  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ , etc.) The ions leave the suppressor and enter the detector, a conductivity meter. As they are now in their acid form, they give a strong linear response.

### 3. Scope

- 3.1 The detection limit is reported in the individual method.

## 4. Interferences

4.1 Interferences are discussed in the individual method.

## 5. Apparatus

5.1 Dionex model 2020i ion chromatograph equipped with:

5.1.1 Spectraphysics 4270 computing integrator.

5.1.2 130  $\mu$ L sample loop.

5.1.3 Guard column, 4mm x 50mm, 37042 AG4A.

5.1.4 Separator column, 4mm x 250 mm, 37041 AS4A.

5.1.5 Micro membrane suppressor, 38019, or electrolytic suppressor.

## 6. Reagents

6.1 High-purity, distilled and deionized water.

6.2 Standard eluent (0.0025 M  $\text{NaHCO}_3$ , 0.002M  $\text{Na}_2\text{CO}_3$ ): dissolve 0.84 g  $\text{NaHCO}_3$  and 0.848 g  $\text{Na}_2\text{CO}_3$  and make up to four litres with distilled water.

6.3 Regeneration solution (25mN  $\text{H}_2\text{SO}_4$ ): dissolve 2.775 ml of conc.  $\text{H}_2\text{SO}_4$  and make up in 4 litres of water.

6.4 Stock standards: see individual anion methods.

## 7. Procedure

## 8. Precision and Accuracy

## 9. Calculations

All the above are discussed in the individual anion methods.

## 10. References

10.1 Ion Chromatographic Analysis of Environmental Pollutants, Vol. I & II, by E. Sawicki and J.D. Mulik, Ann Arbor Science.

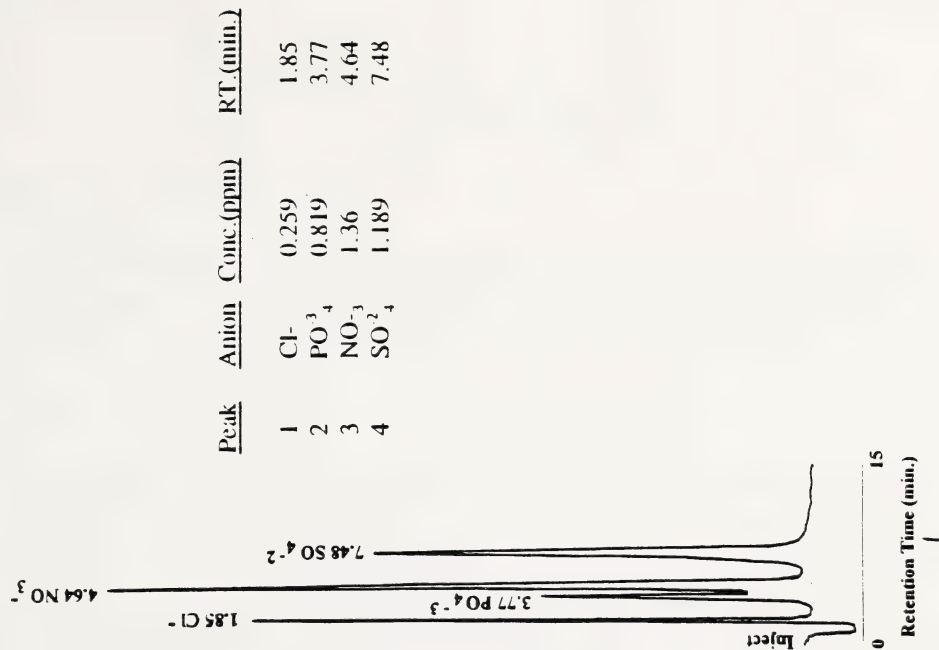
10.2 Ion Chromatography Manual, Dionex Corporation.

Figure 1. Chromatogram of Standard Anions

Instrument Conditions

Eluent 0.0025N NaHCO<sub>3</sub>/0.002 N Na<sub>2</sub>CO<sub>3</sub>  
 Flow Rate 2 mL/min  
 Guard Column 3 x 25 mm  
 Separator Column 3 x 250 mm  
 Suppressor Micromembrane  
 Injection Volume 124 mL  
 Meter Full Scale 3 µ MHO

Conductivity  
 Detector  
 Response





APPENDIX E  
CATIONS, DISSOLVED (ION CHROMATOGRAPHY)  
METHOD 52626





## CATIONS, DISSOLVED

(Ion Chromatography)

### 1. Introduction

- 1.1 Ion chromatography is capable of measuring very low concentrations, which makes it particularly well suited for precipitation analysis. Sodium, ammonium, potassium, calcium, and magnesium cations can be analyzed in a single 15-minute run.

### 2. Principle

- 2.1 Like other chromatographic techniques, ion chromatography consists of a stationary phase and mobile phase. The equilibrium of each ion between the two phases governs the amount of time that the ion is retained in the column. Those ions with the least affinity for the exchange site are carried through first by the eluent stream.
- 2.2 The technique consists of injecting the sample by means of a sample loop into the mobile phase. The eluent carries it sequentially through a separator column, a suppressor column and a conductivity detector.
- 2.3 The eluent for cations is dilute acid (30 mM HCl). The separator is a pellicular cation exchange resin which has an affinity for cations in the following order  $H^+ < Na^+ < NH_4^+ < K^+ < Mg^{++} < Ca^{++}$ . When the eluent carries the sample through the separator, the ions with greater affinity are retained longer in the column, thus effecting a separation. They leave the separator as chloride salts and then enter the suppressor. The suppressor, which contains a micromembrane, has the function of removing background conductivity caused by the eluent. It accomplishes this by exchanging the chloride ions for hydroxyl ions. This converts the highly conducting  $H^+Cl^-$  to  $H_2O$ , which has a low conductivity. It also converts all the ions of interest ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{++}$ ,  $Ca^{++}$ ) to their hydroxide form. They leave the suppressor and enter the detector, a conductivity meter. Because they are now in the hydroxide form, the response is very sensitive, with excellent linearity.

### 3. Scope

- 3.1 The detection limit for each cation is reported in the individual method.

#### 4. Interferences

4.1 Interferences are discussed in the individual method.

#### 5. Apparatus

5.1 Dionex model 2020i or Dx-300 ion chromatograph equipped with:

5.1.1 200  $\mu$ L sample loop.

5.1.2 Guard column, 4mm x 50mm, 44002, CG12.

5.1.3 Separator, 4mm x 250mm, 44001, CG12.

5.1.4 Micromembrane suppressor, 37076.

#### 6. Reagents

6.1 High-purity distilled and deionized water.

6.2 Stock HCl (0.6N): add 25 mL conc. HCl and make up to 500 mL with water.

6.3 Standard cation eluent (0.020N): add 66.7 mL of conc. HCl to water and dilute to 2 litres.

6.4 Regeneration solution (0.02N) KOH: add 1.122 g of KOH and make up to 1 litre with water.

6.5 Regeneration solution: when auto-regeneration cartridge 39563 is used (0.10M tetrabutyl ammonium hydroxide), add 65.53 mL of 40% tetrabutylammonium hydroxide and make up to 1 litre with water. (Prepare 0.1M tetrabutylammonium hydroxide can be purchased from Dionex.

6.6 Standard stock solutions are discussed in the individual method descriptions.

#### 7. Procedure

Precision and Accuracy

Calculations

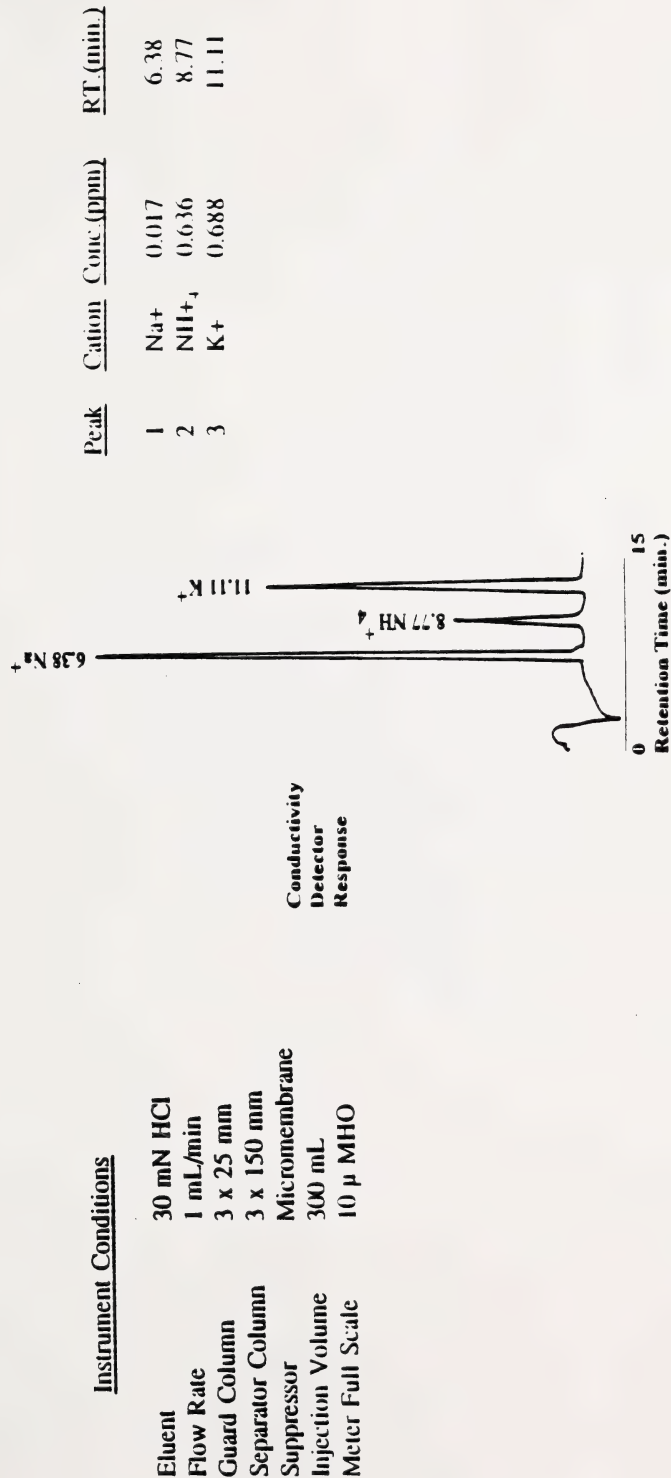
7.1 All the above are discussed in the individual cation methods.

#### 8. References

8.1 Ion Chromatographic Analysis of Environmental Pollutants. Vol. I & II, by E. Sawicki and J.D. Mulik. Ann Arbor Science.

8.2 Ion Chromatographic Manual, Dionex Corporation.

Figure 1. Chromatogram of Standard Cations











## SECTION 5

Technology Evaluation  
and Chemical Analysis,  
Progress Report 1991-1992



ACID DEPOSITION PROGRAM

TECHNOLOGY EVALUATION  
AND CHEMICAL ANALYSIS  
PROJECTS

PROGRESS REPORT TO  
MARCH 31, 1992

Eric Peake  
Environmental Research and Engineering Department  
Alberta Research Council  
3rd Floor, 6815 - 8 Street NE  
Calgary, Alberta, T2E 7H7  
Canada  
March, 1992





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## LIST OF APPENDICES

Appendix 1. Project management plan.

Appendix 2. Acid Deposition Program protocol document. (Report Appended)

Appendix 3. A Comparison of methods for calculating effective acidity (EA) based on Alberta data. (Report Appended)

## ABSTRACT

The objective of the Technology Evaluation project within the ADP is to evaluate equipment and methodology for monitoring dry acidic deposition and to make recommendations for its application within an acid deposition monitoring network. The Chemical Analysis project is to provide laboratory support to the Technical Evaluation project and to transfer technical and analytical experience gained during the ADRP to the ADP.

The focus of the program during the 1991/92 fiscal year was on the establishment of a prototype dry deposition station at Royal Park, Alberta and on the testing of equipment at that site. Related aspects were a preliminary examination of criteria for estimating deposition velocity and the establishment of procedures for data collection and handling. Questions regarding the use of the effective acidity concept as a possible means of establishing limits for acid deposition in the province were raised by the Management Committee were addressed in part.

The prototype monitoring station was installed and equipped with annular denuder-filter pack systems to sample atmospheric pollutants on a six-day integrated basis and on randomly selected days. The mean concentrations of pollutants measured over the two sampling periods were similar, the six-day averages being: for the gases  $\text{SO}_2$ , 8.98  $\mu\text{g}/\text{m}^3$  (as  $\text{SO}_4^{2-}$ );  $\text{HNO}_2$ , 0.22  $\mu\text{g}/\text{m}^3$ ;  $\text{HNO}_3$ , 0.78  $\mu\text{g}/\text{m}^3$ ; and  $\text{NH}_3$ , 1.71  $\mu\text{g}/\text{m}^3$ . The  $\text{SO}_2$  value corresponds to 2.0 ppb in the atmosphere, and given a deposition velocity of  $0.7 \mu\text{m s}^{-1}$  to a dry deposition of 20 kg/ha/y as  $\text{SO}_4^{2-}$ . The particulate concentrations were:  $\text{SO}_4^{2-}$ , 0.87  $\mu\text{g}/\text{m}^3$ ;  $\text{NO}_3^-$ , 2.22  $\mu\text{g}/\text{m}^3$ ; and  $\text{NH}_4^+$ , 1.37  $\mu\text{g}/\text{m}^3$ . The  $\text{NO}_3^-$  value was skewed by one data point. These values are higher than <sup>these</sup> measured during the ADRP at Fortress Mountain and in remote areas of southern California. They are comparable to concentrations measured near Crossfield and lower than measurements made in central Germany. The  $\text{HNO}_3$  concentrations were higher than at Crossfield but considerably lower than in the San Bernardino mountains of southern California. Results could not be compared with those from the CAPMoN filter system which has yet to be installed.

The Chemical Analysis support program was conducted using facilities at the University of Calgary. A technician was trained in the preparation and analysis of annular denuder systems for use in the Technology Evaluation program. Methods were established and an ADP Protocol Document was written. This portion of the program is to be transferred to the AEC effective April 1, 1992.

Meteorological data, required to permit the calculation of the aerodynamic and boundary layer resistances and make estimates of the deposition velocity, was not available at the Royal Park site. A simple computer program to calculate  $R_a$  and  $R_b$ , using the approach of Hicks, was developed and tested with data collected during the ADRP. The results will be compared with those using from other equations, and the most appropriate method will be selected for use in an Alberta dry deposition network.

The needs of the dry deposition monitoring network were considered in the design of a new air quality monitoring data base ensuring that the data produced by the network will be compatible with the new data base. ADRP data is being reformatted to make it compatible with the new data base.

Questions about effective acidity were raised by the Management Committee and addressed in a report entitled "A comparison of Methods for Calculating Effective Acidity (EA) Based on Alberta Data". The need for a sensitivity analysis of factors contributing to EA was expressed at a workshop on this topic, and a computer program has been developed to assist in this analysis.

In summary: the Chemical Analysis project has been brought to a successful conclusion; substantial progress has been made toward meeting the objectives of the Technology Evaluation project with problems in obtaining equipment delaying its completion; and progress has been made in evaluating effective acidity as a possible criteria for setting acidic deposition limits in the province. This evaluation of EA was not part of the original objects.





## THE ACID DEPOSITION PROGRAM TECHNOLOGY EVALUATION AND CHEMICAL ANALYSIS PROJECTS

### 1.0 OBJECTIVES

The major objective of this portion of the ADP is to monitor dry deposition in Alberta so as to determine current loadings, spacial patterns and temporal trends and to measure and predict changes in dry deposition resulting from changing emission patterns.

#### 1.1 Technical Evaluation Project

The objective of the Technology Evaluation project within the Acid Deposition Program is to evaluate equipment and methodology for monitoring dry acidic deposition and to make recommendations for its application within an acid deposition monitoring network. Sub objectives of the project are: (i) To transfer the technical and analytical experience gained during the Acid Deposition Research Program to the Acid Deposition Program. (ii) To develop, install and operate a prototype dry deposition monitoring station. (iii) To develop a detailed quality control and quality assurance protocol for instrument operation and data collection procedures. (v) To evaluate, under Alberta conditions, the filter pack (FP) and the filter pack-annular denuder (FP-AD) sampling systems by collecting dry deposition data for one full year. (vi) To develop an overall experimental design having appropriate sampling and statistical methods for use in the monitoring network.

#### 1.2 Chemical Analysis project

The objective of the Chemical Analysis project is to provide laboratory support for the Technical Evaluation project by preparing and analyzing the AD-FP systems and by analyzing samples collected by FP.

### 2.0 INTRODUCTION

The purpose of the Acid Deposition Program, as defined in the "Acid Deposition Program Action Plan" is to implement the Acid Deposition Management Strategy for Alberta and to respond to the recommendations of the Acid Deposition Research



Program, the Interim Acid Deposition Critical Loadings for Western and Northern Canada Report, and the Three Year Report of the Western and Northern LRTAP Committee. The objectives of the program are: (i) To provide scientific and technical knowledge for limiting acid deposition to protect sensitive forest, lake and soil systems in Alberta. (ii) Monitor wet and dry deposition of acidic substances in priority areas of the Province; and (iii) Establish reliable methods for protection from acid deposition in Alberta.

Some elements of the ADP are shown in Figure 1. The concept of "effective acidity" has been proposed as one means of quantifying the potential ecosystem effects of acid deposition and for setting acidic deposition limits in Alberta (Alberta Environment, 1990). Effective acidity is a method of estimating the degree of acidification, in strong acid equivalents, which a soil would experience as a result of atmospheric inputs. The estimation of effective acidity (or any other measure of the ecological effects of atmospheric pollutants) depends upon monitoring of acid, or acid forming, atmospheric inputs in the form of wet deposition, as rainfall, snow or fog and dry deposition, as gases and particles. The focus in the past has been on wet deposition, primarily because precipitation samples could be collected and analyzed for their chemical composition with available methodology. Also most studies were conducted in Eastern North America where wet deposition was of greater significance than dry deposition.

Over the past decade the importance of dry deposition has gradually been recognized. In Western North America dry deposition is believed to predominate, although measurements are few. With the recognition of the importance of dry deposition has come the need to develop methodology suitable for it's measurement. There are no simple direct methods for measuring dry deposition (Hicks 1987); two approaches are generally used. The first approach is to carefully analyze the chemistry of exposed surfaces such as leaves or surrogate surfaces; the second is to infer dry deposition fluxes from the atmospheric concentrations of the pollutants in question using the concept of deposition velocity. The equation  $-F = C \times V_d$  describes this process, with F being the flux away from the surface (thus flux toward the surface is -F), C the atmospheric concentration of the species of interest, and  $V_d$  it's deposition velocity. Because of the difficulties inherent in obtaining representative natural surfaces or surrogate surfaces for

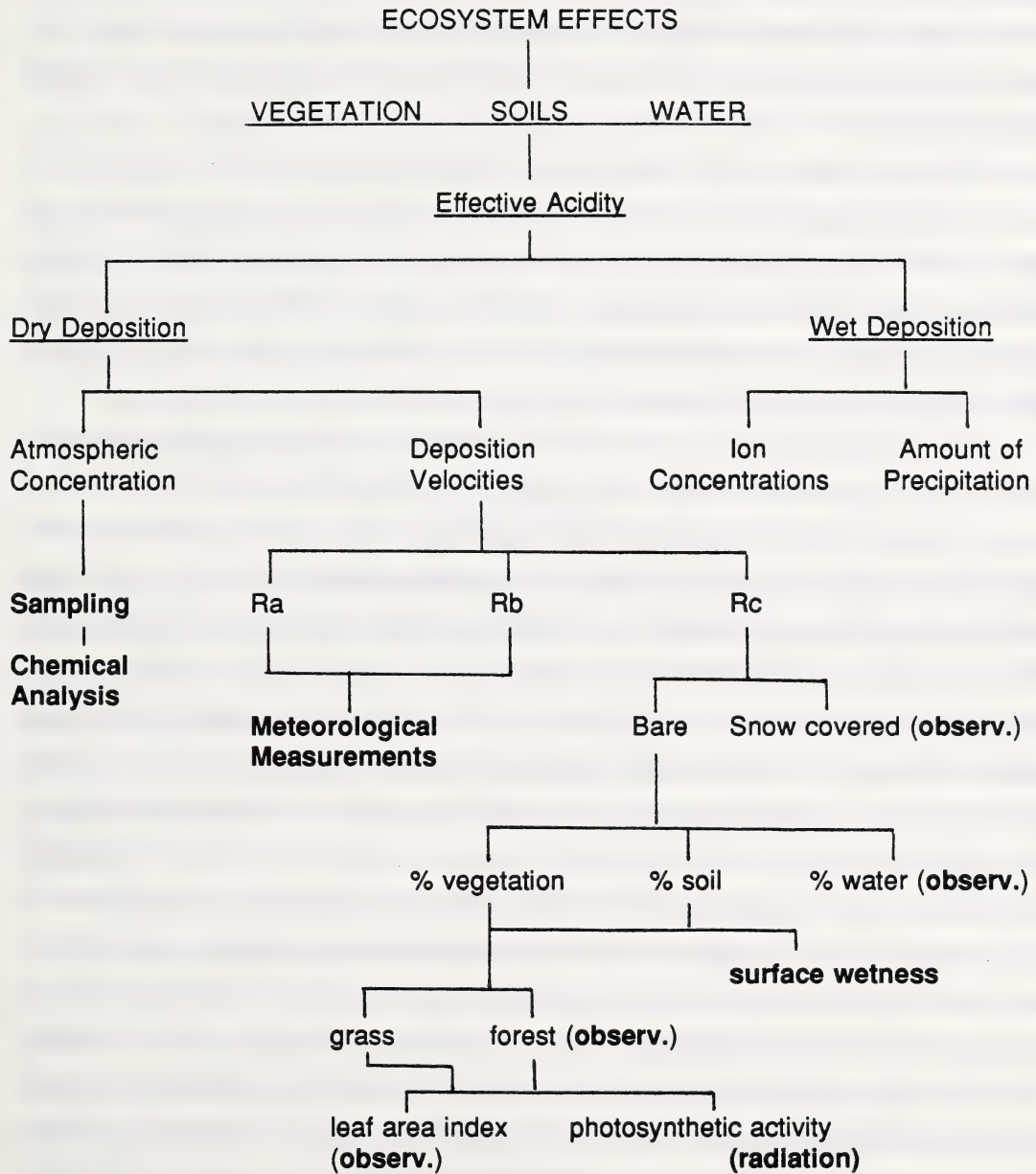


Figure 1. Elements of the Acid Deposition Program.

chemical analysis, the latter approach, which requires the measurement of atmospheric concentrations and characteristic deposition velocities has been more widely used. The measurements and observations required to estimate dry deposition are shown in bold letters in Figure 1.

Continuous monitors for measuring the atmospheric concentration of acidic and acid forming gases in the vicinity of major sources of emissions are available but generally lack sufficient sensitivity to measure concentrations away from these sources. Alternate methods have been applied, ranging from simple filtration devices to collect samples for subsequent chemical analysis to tuneable diode lasers for monitoring atmospheric nitric acid concentrations.

The two most commonly used sampling devices are a three stage filter pack (FP), which is used to collect particles, nitric acid, and sulphur dioxide, and the combined annular denuder filter pack system (AD-FP), which consists of three annular denuder tubes to collect nitric acid, nitrous acid, sulphur dioxide and ammonia, and a two stage filter pack, which is used to collect fine particles and volatilized ammonium nitrate. The FP has the advantage of simplicity of operation and is used in the Canadian Air and Precipitation Monitoring Network. The AD-FP provides more information on the chemical species of interest in evaluating the acidifying effects of dry deposition and has been widely used in US research programs. Of prime importance in evaluating the merits of these sampling systems in the Technology Evaluation project is their cost effectiveness in providing the information required for the setting and monitoring of target loading standards for Alberta. In response to the need for monitoring, a network of air chemistry observation stations, equipped for both wet and dry deposition monitoring, are to be developed within the ADP using state of the art sensing and data acquisition systems.

The second parameter which must be determined in order to estimate the amount of dry deposition of an acidic species is its deposition velocity. Deposition velocities depend not only upon the chemical and physical properties of the gas (or particle) but also upon meteorological conditions and upon the nature and condition of the surface; whether it is agricultural soil, grassland, forest, lakes, snow covered, wet or dry. Several methods have been used to measure deposition velocities to uniform surfaces such as



grasslands, forest and snow, but all are limited in their application, are expensive, and are not suitable for routine use in a monitoring network. Measurements have been made in Alberta using the gradient method which relies upon highly sensitive monitoring equipment to measure differences in concentration of from 0.2% to 5% with a precision of better than 10%. With atmospheric concentrations of SO<sub>2</sub> in Alberta generally being less than 10 ppb, such measurements are rarely possible. The Atmospheric Environment Service has used the eddy diffusion method to measure deposition velocities of ozone and SO<sub>2</sub> at selected sites in Eastern Canada with an estimated uncertainty of 20%. These types of measurements only be made over uniform terrain and are site specific.

The inferential approach to estimating deposition velocity is based upon an analogy to an electrical circuit with:

$$V_d = \frac{1}{R_a + R_b + R_c}$$

The resistance to deposition is divided into three components; the aerodynamic resistance,  $R_a$ ; the boundary layer resistance,  $R_b$ ; and the canopy resistance (or surface resistance),  $R_c$ . Approximate values for  $R_a$  and  $R_b$  can be calculated from meteorological measurements of the wind profile, and the standard deviation in wind direction (Hicks et al, 1985). Because these parameters are influenced by atmospheric stability, measurements of temperature and wind profile to a height of at least 10m are required.

The surface resistance,  $R_c$ , often dominates the deposition velocity calculation. It is generally inferred rather than measured and can vary greatly; from zero for a wet or alkaline surface to 1000 s cm<sup>-1</sup> for smooth, snow covered surfaces. Because  $R_c$  is a function of the condition of the surface it can change rapidly, depending, in part, on whether the surface is wet or dry. For vegetated surfaces,  $R_c$  depends upon the stomatal resistance and the leaf mesophyll resistance which are affected by humidity, temperature, and solar radiation. As a result  $R_c$ , and  $V_d$ , show strong diurnal variations. Estimates of  $R_c$  require observations of the degree to which the land within about one km of the measurement site is covered with vegetation, agricultural soil, or lakes, as well as the surface wetness and the degree of plant activity (Figure 1).

The Technology Evaluation project addresses the first task outlined in the Technology part of the Acid Deposition Program Action Plan, to develop a reliable dry deposition monitor for gases, aerosols and for fine particles. To a lesser extent it also addresses the estimation of effective acidity and deposition velocity.

### 3.0 WORK PLAN

A project work plan was designed for the Technology Evaluation project and the supporting Chemical Analysis project with links to the Data Management Project (Appendix 1). The plan provides coordination of the activities of the major participants in the ADP; the Alberta Environmental Centre (AEC), the Environmental Quality Monitoring Branch (EQMB), and the Alberta Research Council (ARC). It focuses on the installation and operation of the prototype monitoring station, the collection and chemical analysis of atmospheric samples, the compilation and evaluation of results, and recommendations for the establishment of the dry deposition monitoring network. The activities of the major participants are interdependent and the successful and timely completion of the project depends upon their close cooperation.

### 4.0 PROTOTYPE MONITORING STATION

#### 4.1 Site Description

A site for the prototype acid deposition monitoring station was selected by the AEC based on the criteria for sampling station locations used by the EQMB. The station is located in an agricultural area near Royal Park, Alberta, about 10 km northwest of Vegreville. It is situated on a slight rise of land in a hay field, about 300m from the nearest trees and 400m from the nearest county road. Regional sources of atmospheric pollutants are petroleum refineries and associated facilities near Edmonton, 90 km to the west and similar facilities at Redwater, 80 km to the west. Fertilizer and other industrial plants are located at Fort Saskatchewan 80 km to the northwest. At Wabamum, 75 km to the west of Edmonton are the coal fired power generating plants. The city of Edmonton and its adjacent towns of St. Albert and Sherwood Park are also major sources of nitrogen oxides from motor vehicles emissions. Local sources of pollutants are



agricultural; from cattle production and fertilizer application. The station is readily serviced from the AEC at Vegreville but is sufficiently far from the town so as not to be directly influenced by local emissions. Its location is representative of the region.

The AEC leased the land, obtained and installed on site a trailer to house the monitoring equipment, arranged for power and telephone service, and installed the sampling and meteorological towers, completing items 1,2,5,9,10,13,40,43,44,45,51, and 54 of the project management plan.

#### 4.2 Monitoring Equipment

Equipment to be operated at the station includes two standard filter pack systems, as used by the Atmospheric Environment Service, and two annular denuder-filter pack systems, as well as meteorological monitoring equipment and precipitation samplers. The sampling equipment is to be controlled by a data logger which stores flow control and meteorological data. This equipment, together with a computer for the Data Management project, and a micro balance for the Chemical Analysis project, was ordered by the EQMB (project management items 21-31). Existing flow control and timing equipment for the AD-FP systems was modified by the ARC and two AD-FP systems were installed on the sampling tower (project management items 8, 11, 12, 13, and 41). The EQMB encountered difficulties in obtaining some parts of the FP systems and the data logger, furthermore the data logger has failed to operate to the standards of the EQMB and has been repeatedly returned to the factory. As a consequence, installation of the FP and meteorological systems by the EQMB has been delayed and the two AD-FP systems are being operated without the data logger control system. The filter pack systems have not yet been installed thus no field data has been collected with these systems. The date set for reaching the primary objective of evaluating and comparing the two sampling systems, and making recommendations for the type of equipment to be installed in the dry deposition monitoring network, has been delayed.

## 5.0 MEASUREMENTS AT ROYAL PARK USING AD-FP SYSTEMS

### 5.1 Methodology

#### 5.1.1 The Annular Denuder-Filter Pack Sampling System

The combined annular denuder-filter pack sampling system (AD-FP) is designed to separate and collect acidic gases ( $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{HNO}_2$ ), basic gases ( $\text{NH}_3$ ), and fine particles from the ambient atmosphere. The AD-FP sampling unit consists of a cyclone, a series of three annular denuder tubes, and a filter pack, assembled in a rigid housing. The unit is mounted on a sampling tower and connected to a vacuum pump, flow controller, and data logger housed in an air quality monitoring trailer. Ambient air is pulled through the sampling unit by the vacuum pump with the flow being regulated, and monitored, by the mass flow controller. The data logger is to control the start and length of the sampling period and record air flow through the unit. The collected gases and fine particles are chemically analyzed and, from the recorded sampling rate, the concentration of these pollutants in the atmosphere is determined. Details of the design, function, and operation of the AD-FP system are contained in the Acid Deposition Protocol Document which was written as part of this Technology Evaluation project.

#### 5.1.2 Sampling Schedule

A well-designed, statistically-sound, sampling strategy is a key component of an environmental monitoring program. The sampling schedule for the prototype monitoring station was designed to allow the performance of the filter pack and annular denuder-filter pack sampling systems to be evaluated on a statistically-valid basis and to provide the maximum information on the daily, weekly, and seasonal variability in concentrations of atmospheric pollutants. The number of samples to be collected could not exceed the capabilities of the laboratory to prepare the sampling systems and to chemically analyze the collected samples. Zack Florence of AEC proposed an experimental design in which pollutants would be sampled within random time intervals of equal length. One filter pack and one AD-FP sampler was randomly assigned to a continuous 6-day cycle during which each sampler collects an integrated 6-day sample. A second filter pack and AD-FP system both sample for the same randomly selected 24-hour period within each 6-day

6-day period. The start of the 6-day periods was chosen to coincide with the US NAPAP program. The two AD-FP systems installed at Royal Park began operating on this schedule in November of 1991.

#### 5.1.3 Field Operation

Details of the installation, operation, and quality control procedures for the AD-FP units are contained in the Acid Deposition Protocol Document. The filter packs contained in the AD-FP sampling units are assembled, and the annular denuder tubes are coated, in laboratories at the University of Calgary. These components are shipped by courier to the AEC laboratory in Vegreville where they are assembled into the sampling units. The AEC is responsible for the installation of the sampling units, the setting of the sampling periods, and the shipping of the units to the University of Calgary laboratory for chemical analysis. At the Royal Park prototype dry deposition monitoring station each of the sampling units is attached to the appropriate flow control system for either 6-day or 24-hour sampling and raised to a height of 10 meters on the sampling tower. The timers for each of the sampling systems are set according to the instructions contained in section 1.11 of the Acid Deposition Protocol Document. (Note the timers presently in use were designed for a different function. The data logger will eventually control the sampling period.) Once the sampling period is complete, the units are disconnected from the flow control system, returned to the AEC, disassembled, and the filter packs and annular denuder tubes shipped by courier to the University of Calgary for analysis.

#### 5.1.4 Chemical Analysis

The ARC, through an existing contractual agreement with the University of Calgary for cooperation and use of facilities, arranged for the preparation of annular denuder tubes, the chemical analysis of tubes and filters, and the supervision and training of a technician hired by the AEC. Training of the technician in laboratory procedures, in the use of the required analytical instrumentation, and in the preparation of sampling systems began in September, 1991 and progressed satisfactorily. Methodology was established and schedules were prepared for the preparation and analysis of sampling systems. Quality control procedures were implemented. Details of the methods are contained in the Acid Deposition Protocol Document. Laboratory services in support of the ADP are to be



moved to the AEC in Vegreville as of March 31, 1992.

#### 5.1.5 Calculations and Data Handling

Sampling information and data from the chemical analysis of the AD-FP sampling units is entered into the Excel spreadsheet as shown in the example in Figure 2. The spreadsheet uses information typed into the outlined areas to calculate micrograms of each species collected on each tube or filter. The spreadsheet also calculates micrograms of each species per cubic metre of ambient air as well as concentrations of gaseous  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$ , and concentrations of particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  in the ambient atmosphere. The format is compatible with the data base developed for the ADP as part of the data management project.

### 5.2 Results and Discussion

#### 5.2.1 Field Sampling Program

The field sampling schedule showing those periods for which samples were successfully collected and analyzed is given in Table 1. The results from samples collected or analyzed after March 1, 1992 are not included in this report. Continuous 6-day samples have been collected since November 18, 1991. Breakage of tubes during shipment, which occurred at the beginning of the program, was overcome by shipping the components rather than the assembled AD-FP units. Concerns about possible contamination caused by this method of shipping proved to be unfounded. Analysis of laboratory versus field blanks showed no statistical differences (see section 5.2.2.1 on quality control). Difficulties were encountered with the timer for the 24-hour sampling periods. Upon analysis, three of the units which had been installed at Royal Park, were found not to have been exposed. These samples were treated as unintentional field blanks and are included in the quality control data. Control of the sampling periods by the data logger future will eliminate future problems.

#### 5.2.2 Analytical Results

The results of the chemical analysis of the AD-FP systems are shown on the spreadsheet outputs contained in Appendix 2 and tables of summarized data extracted from the spreadsheets are presented in the following sections.

Site	Royal Park	Date of Analysis	Feb 19/92	File No.	Fe0692w	Sample #	AD 1 -p45
Sampling Per. (hrs)	144	(24 , 144, blank, etc)	Flow Rate (lpm)	7		Total Vol.	60.48 cubic m.
Start time	0	0 (Hour:Minute)	Stop time	24	0	0 (Hour:Minute)	
Start Date	2	6 92 (Month:Day:Year)	Stop date	2	11 92	(Month:Day:Year)	
Date	Feb 19/92	NO2 NO3 SO4	Date	Feb 20/92	NO2 NO3 SO4	NH4	
Resp. Factor "a"	3.3163	3.81 -2.3853	Resp. Factor "a"			-0.54	-0.4889 0.02272
Resp. Factor "b"	0.9627	1.1697 0.8506	Resp. Factor "b"			1.1639	0.8622 0.02251
<div> <div>T1 NO2 T1 NO3 T1 SO4</div> <div>T2 NO2 T2 NO3 T2 SO4</div> <div>Te NO3 Te SO4 Ny NO3 Ny SO4</div> </div>							
Date of Analysis	Feb 12/92		Feb 19/92		Feb 20/92		
Extraction Vol. (mL)	10	10	10	10	20	20	10
Dilution	10	10	1	10	10	10	1
Peak Area	49.25	293.95	411.6	449.1	160.6	148.6	520.3
UG PER SAMPLE	5.07	34.76	347.72	5.29	13.42	34.48	89.62
UG PER BLANK	0.50	0.62	0.93	0.62	0.93	0.21	0.40
UG / M3	0.08	0.56	5.73	0.08	0.21	0.57	1.48

	Te Ca <sup>+</sup>	Te Mg <sup>++</sup>	Te Na <sup>+</sup>	Te K <sup>+</sup>	T3 NH <sub>4</sub> <sup>+</sup>	Te NH <sub>4</sub> <sup>+</sup>	
Date of Analysis	Feb 21/92				Feb 21/92		
Extraction Vol. (mL)	20	20	20	20	10	20	SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup> 5.94 ug per m3
Dilution	1	1	1	1	5	10	HNO <sub>2</sub> 0.07 ug per m3 HNO <sub>3</sub> 0.64 ug per m3
Mg per litre (Peak Ht.)	0.0515	0.0245	0.1135	0.086	22.13	15.69	NH <sub>3</sub> 0.36 ug per m3
UG PER SAMPLE	1.03	0.49	2.27	1.72	26.04	75.18	Particulate SO <sub>4</sub> <sup>=</sup> 1.48 ug per m3
UG PER BLANK					2.83	0.77	Particulate NO <sub>3</sub> <sup>-</sup> 0.98 ug per m3
UG / M3	0.02	0.01	0.04	0.03	0.38	1.23	Particulate NH <sub>4</sub> <sup>+</sup> 1.35 ug per m3
Teflon filter:	initial weight			Final weight			

**Figure 2. Example of laboratory calculations form.**



Table 1. Summary of samples collected at Royal Park and analyzed.

	<u>November</u>			<u>December</u>			
	18-23	26-01	02-07	08-13	14-19	20-25	26-31
Six-Day	XXX	XXX	XXX	XXX	XXX	XXX	XXX
24-hour	X	X					
Blank	X	X	X	X	X	X	X
	<u>January</u>				<u>February</u>		
Period	01-06	07-12	13-18	19-24	25-30	31-05	06-11
Six-day	XXX		XXX	XXX	XXX	XXX	XXX
24-hour	X	X	X	X	X	X	X
Blank	X	X	X	X	X	X	X

#### 5.2.2.1 Quality Control

A second set of annular denuder tubes and filters was prepared with each sampling set and was retained in the laboratory for quality control purposes. The results from the analysis of these "laboratory blank" sample sets is shown in Table 2. Tubes and filter packs were also sent to the Vegreville laboratory and assembled into units which were designated as "field blanks". On three occasions timers at the Royal Park sampling station failed to operate correctly and the sampling units which had been installed were not exposed. These units were designated as unintentional "field blanks". Sixteen of the  $\text{Na}_2\text{CO}_3$  coated annular denuder tubes were analyzed as laboratory blanks and 14 as field blanks. Contamination of the tubes by  $\text{NO}_2$  and  $\text{NO}_3^-$  was small with mean amounts of 0.61 and 0.73 ug per tube respectively, in the laboratory blanks. There was no significant difference between the laboratory and the field blanks, which contained 0.54 and 0.56 ug per tube of  $\text{NO}_2$  and  $\text{NO}_3^-$  respectively. In the case of  $\text{SO}_4^{2-}$ , the mean amount measured on the laboratory blank tubes was 2.83 ug per tube, considerably more than the 0.79 found in the field blanks. Inspection of a quality control chart, Figure 3, showed two outliers in the  $\text{SO}_4^{2-}$  data from the laboratory blanks. These were removed, the laboratory and field blank data was combined, and new mean blank value for  $\text{SO}_4^{2-}$  contamination of 0.95 ug per tube was calculated.

Fourteen blank tubes were analyzed for  $\text{NH}_4^+$  contamination. The mean concentration of  $\text{NH}_4^+$  contamination on the citric acid coated tubes were different between the laboratory and field blank samples, 1.88 and 2.82 ug per tube, respectively. The standard deviation for the field blank data was 3.25 and the quality control chart, Figure 3, showed one outlier. Combining the laboratory and field blank data and removing the outlier reduced the mean to 1.77 ug per tube and the standard deviation to 0.79. Contamination of the Teflon filter with  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ , and the nylon filter with  $\text{NO}_3^-$  was low, with little difference between the laboratory and field blanks. The mean amounts were 0.24, 0.38, 0.56, and 0.60 ug per filter for  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ , respectively. Quality control charts for each ion are presented in Figures 5 to 12. They show no systematic errors in the blank analysis.

Table 2. Quality control blank laboratory and field samples, ug per tube.

	<u>Tubes</u>				<u>Filters</u>			
	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	Te $\text{NO}_3^-$	Te $\text{SO}_4^{2-}$	Te $\text{NH}_4^+$	Ny $\text{NO}_3^-$
<u>Laboratory Blanks</u>								
Mean	0.61	0.73	2.83	1.88	0.24	0.34	0.45	0.76
Number	16	16	16	8	9	9	7	9
Std. Dev.	0.21	0.77	5.06	0.78	0.11	0.22	0.24	0.42
<u>Field blanks</u>								
Mean	0.54	0.56	0.79	2.82	0.24	0.43	0.68	0.41
Number	14	14	14	7	7	7	7	7
Std. Dev.	0.30	0.40	0.32	3.25	0.21	0.14	0.13	0.24
<u>Laboratory and field blanks*</u>								
Mean	0.58	0.65	0.95	1.77	0.24	0.38	0.56	0.60
Number	30	30	28	14	16	16	14	16
Std. Dev.	0.25	0.62	0.56	0.79	0.15	0.19	0.22	0.38

\* Outliers removed.

### Tube SO<sub>2</sub> Quality Control Chart

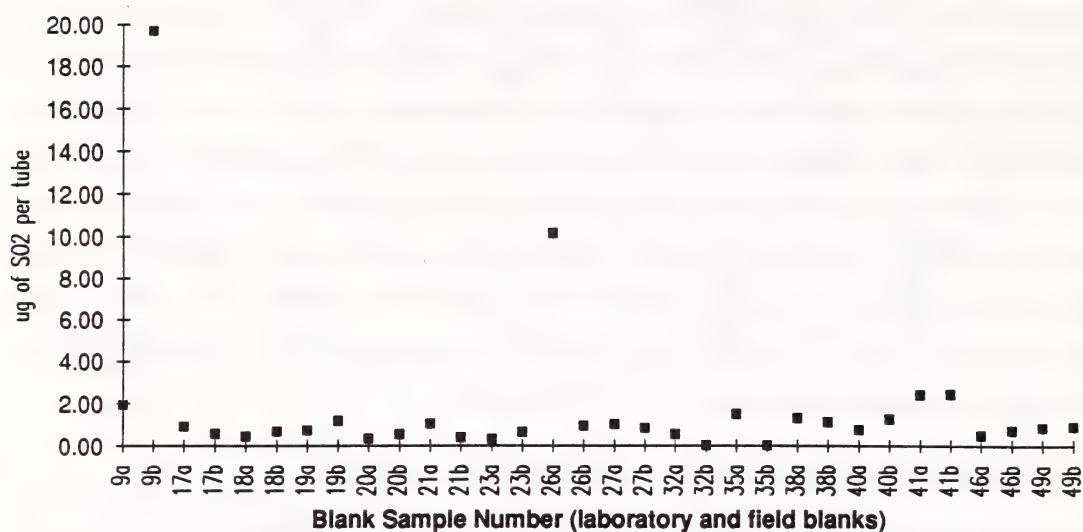


Figure 3. Quality control chart for SO<sub>2</sub> contamination of laboratory and field blank sample tubes.

### Tube NH<sub>3</sub> Quality Control Chart

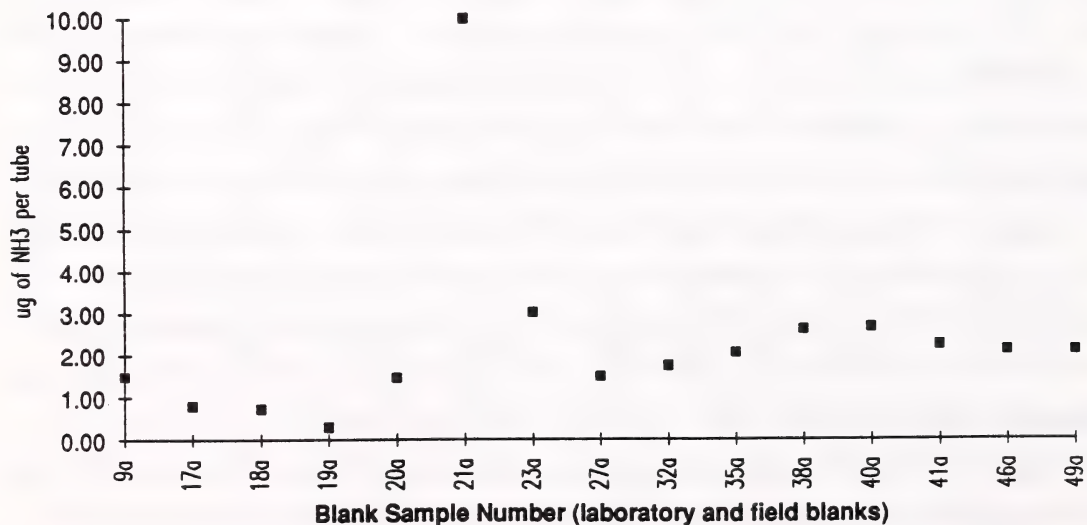


Figure 4. Quality control chart for NH<sub>3</sub> contamination of laboratory and field blank sample tubes.

### Tube NO<sub>2</sub> Quality Control Chart

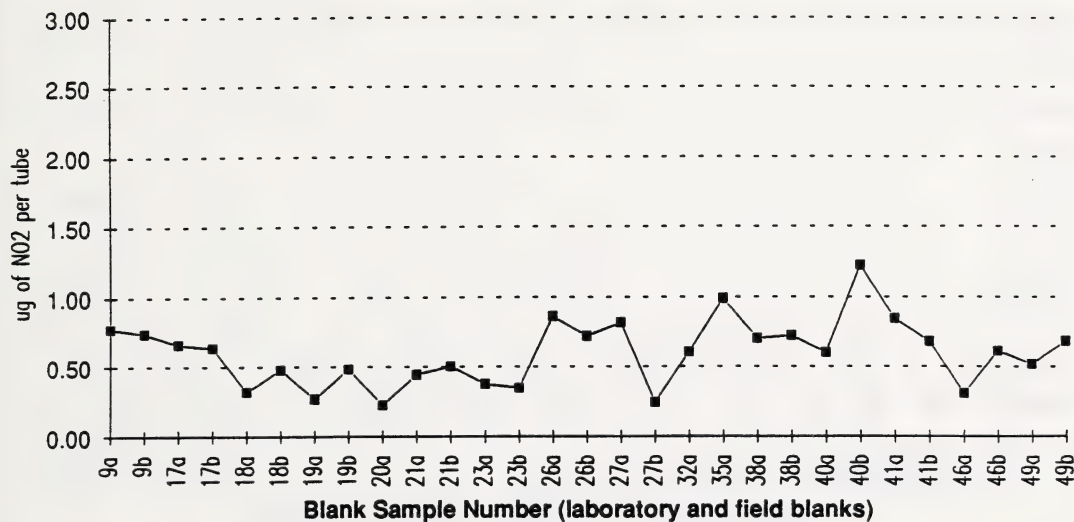


Figure 5. Quality control chart for NO<sub>2</sub> contamination of laboratory and field blank sample tubes.

### Tube NO<sub>3</sub> Quality Control Chart

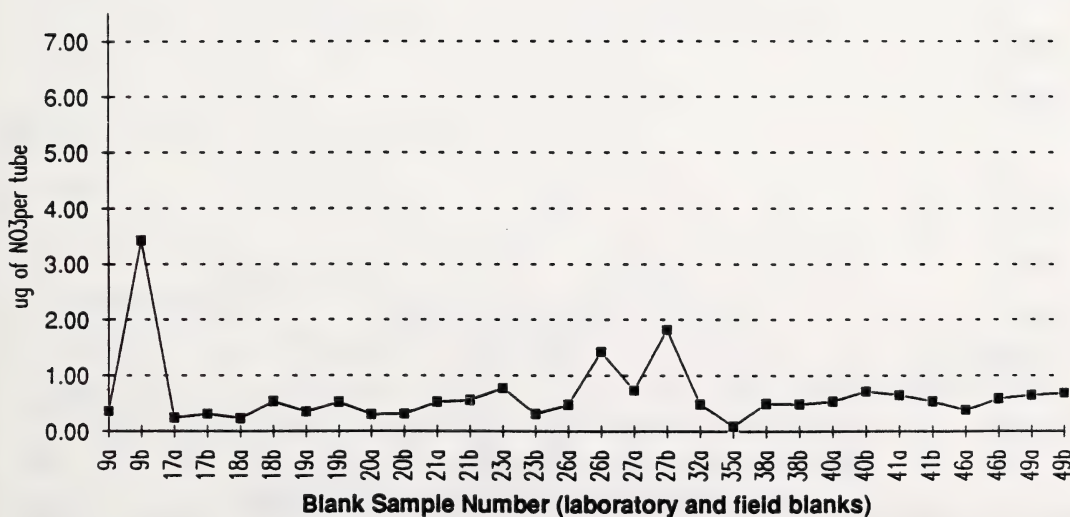


Figure 6. Quality control chart for NO<sub>3</sub> contamination of laboratory and field blank sample tubes.

### Tube SO<sub>2</sub> Quality Control Chart

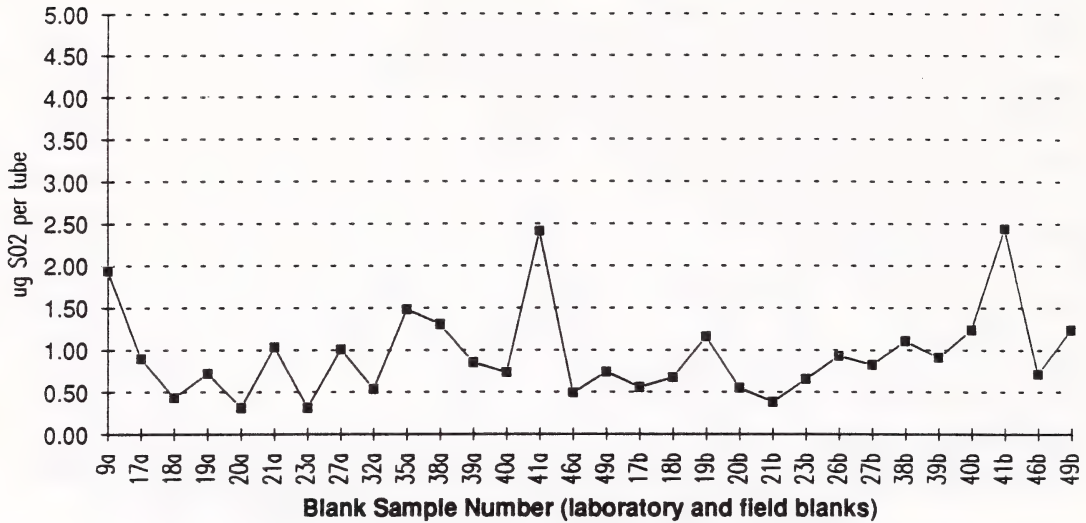


Figure 7. Quality control charts for SO<sub>2</sub> contamination of laboratory and field blank sample tubes.

### Tube NH<sub>3</sub> Quality Control Chart

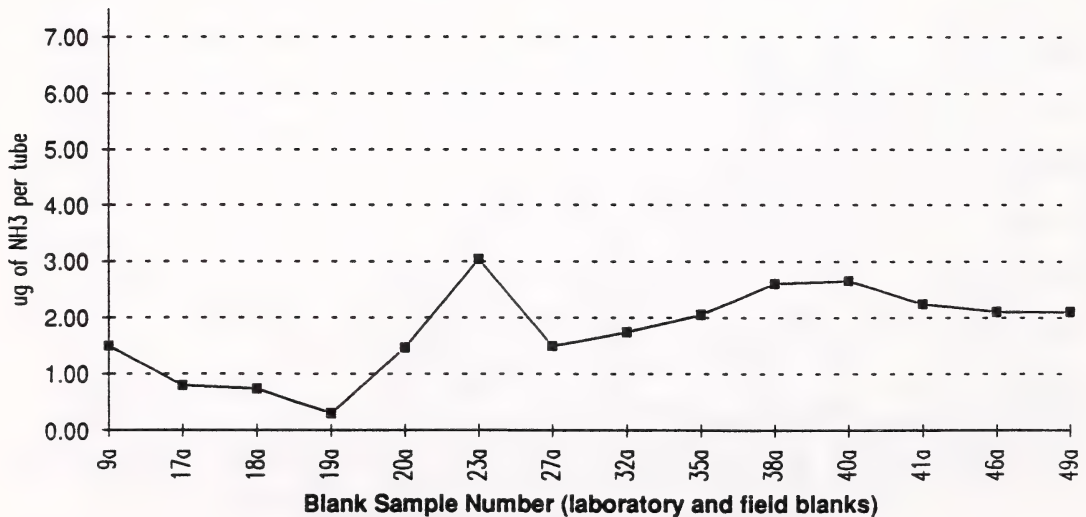


Figure 8. Quality control charts for NH<sub>3</sub> contamination of laboratory and field blank tubes.



### Teflon Filter $\text{NO}_3^-$ Quality Control Chart

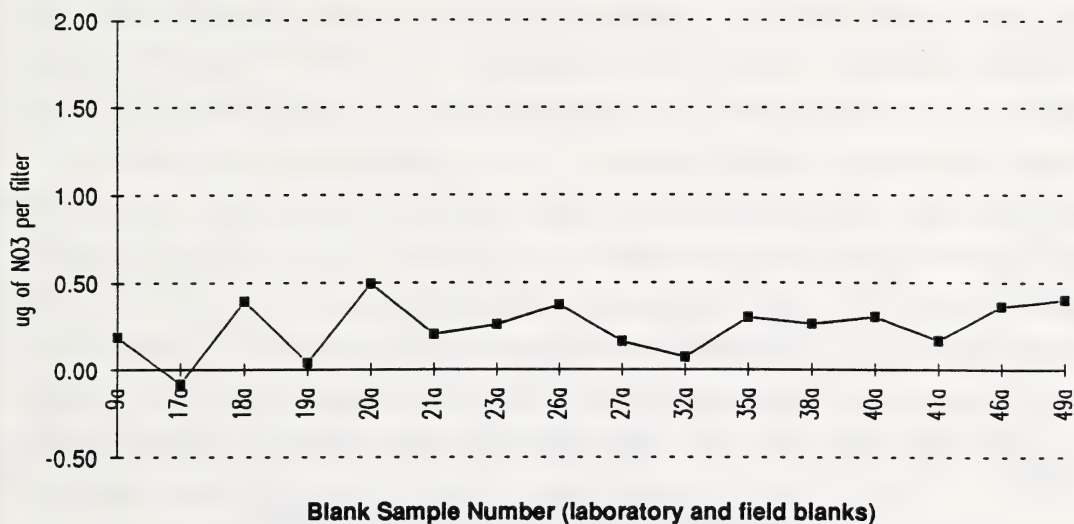


Figure 9. Quality control chart for  $\text{NO}_3^-$  contamination of laboratory and field Teflon filter blank

### Teflon Filter $\text{SO}_4^{2-}$ Quality Control Chart

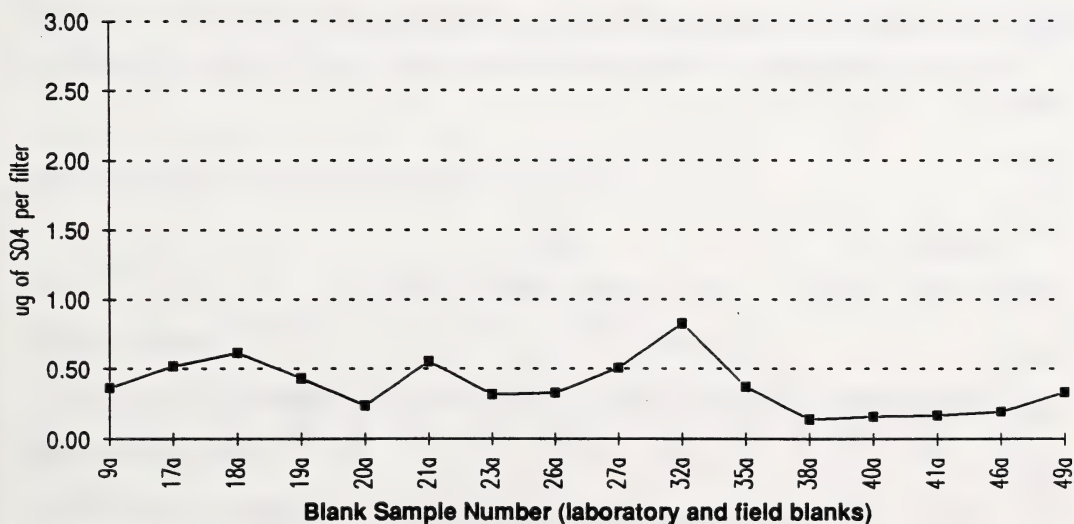


Figure 10. Quality control chart for  $\text{SO}_4^{2-}$  contamination of laboratory and field Teflon filter blank samples.

### Teflon filter $\text{NH}_4^+$ Quality Control Chart

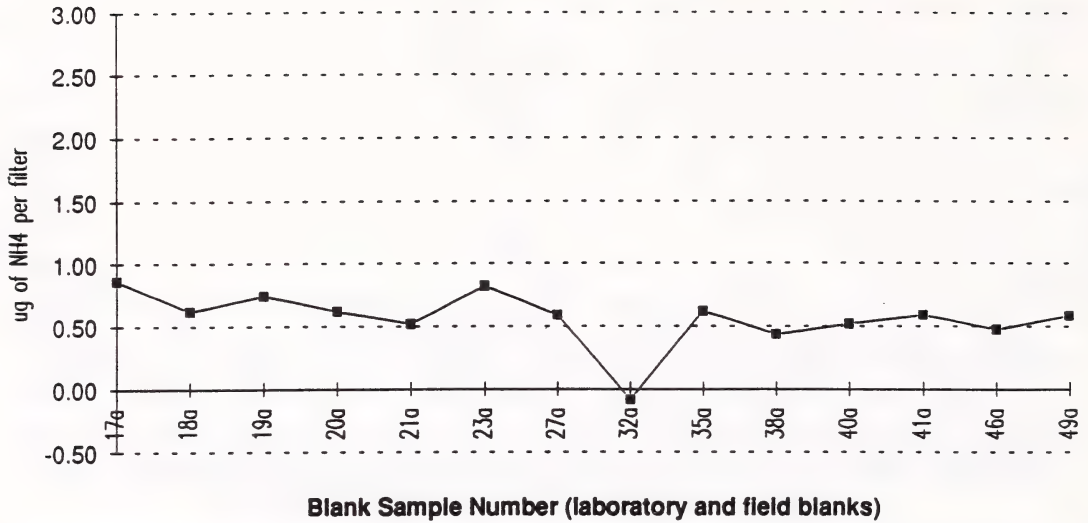


Figure 11. Quality control chart for  $\text{NH}_4^+$  contamination of Teflon filter laboratory and field blank

### Nylon Filter $\text{NO}_3^-$ Quality Control Chart

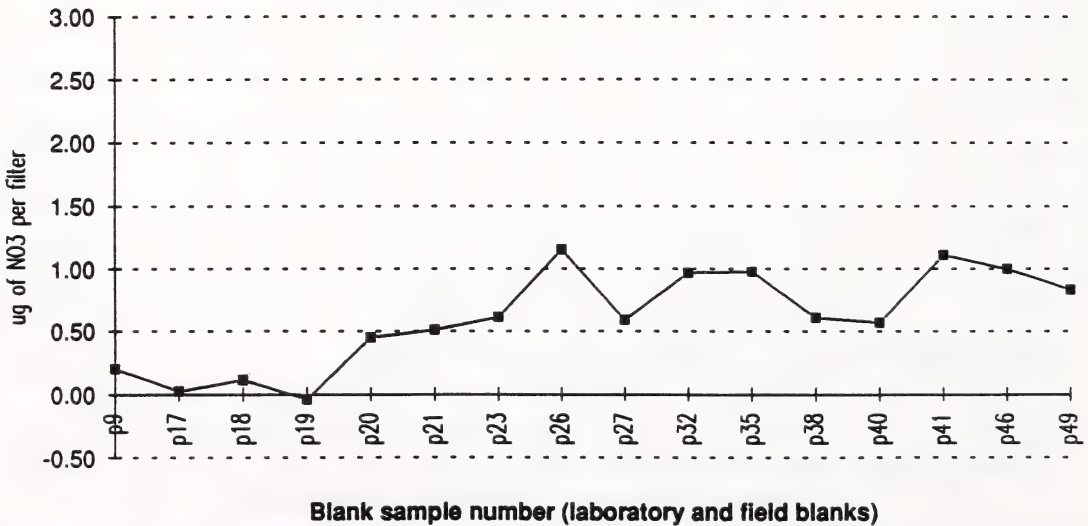


Figure 12. Quality control chart for  $\text{NO}_3^-$  contamination of laboratory and field nylon filter blank samples.

### 5.2.2.2 Detection Limits

The results of the chemical analyses for  $\text{SO}_2$  collected by the annular denuder tubes are expressed in units of  $\mu\text{g}$  of  $\text{SO}_4^{2-}$  per sample. The total amount of  $\text{SO}_4^{2-}$  per sample is  $T1 \text{ SO}_4^{2-} + T2 \text{ SO}_4^{2-} - 2 \times \text{the blank tube } \text{SO}_4^{2-} \text{ value}$ . Thus the concentration of  $\text{SO}_2$  in the atmosphere for a sample collected over a 24-hour period at a flow rate of 7.0 litres per minute would be ( $\mu\text{g}$  of  $\text{SO}_4^{2-}$  collected) divided by 10.08 cubic metres. This value can then be converted to  $\mu\text{g}$  of  $\text{SO}_2$  by multiplying by 0.667, and to part per billion by multiplying by 0.233. Similarly the concentration of nitric acid can be calculated from the amount of  $\text{NO}_3^-$  collected on each of the denuder tubes. The  $\text{Na}_2\text{CO}_3$  coated tubes collect not only nitrous acid from the ambient atmosphere but also a small percent of the ambient  $\text{NO}_2$ . Since the percentage of the  $\text{NO}_2$  collected is small, about 5%, the amount collected on each of the two denuder tubes, is almost identical. To correct for this contamination the amount of  $\text{HNO}_2$  is calculated as  $T1 \text{ NO}_2 - T2 \text{ NO}_2$ .

Several statistical methods have been advanced for calculating the detection limits when sampling using systems such as the AD-FP. The definition of the detection limit as 4.65 times the standard deviation in the analysis of blank samples advanced by Kirchmer (1983) would seem appropriate. Using this criteria and the data from Table 2, the detection limits for major ions were calculated and are presented in Table 3.

Table 3. Detection limits based on quality control blanks.

	<u>Gases</u>				<u>Particle</u>		
	$\text{HNO}_2$	$\text{HNO}_3$	$\text{SO}_2$	$\text{NH}_3$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$
Detection limit ( $\mu\text{g}$ )							
Per Sample	1.18	2.89	2.58	3.65	0.71	0.88	1.04
Detection Limit ( $\mu\text{g}/\text{m}^3$ )							
per 24-h, sampling period	0.12	0.29	0.26	0.36	0.07	0.09	0.10
per 6-day sampling period	0.02	0.05	0.04	0.06	0.01	0.01	0.02

The detection limits for the gases  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{SO}_2$ , and  $\text{NH}_3$  ranged from 1.18 to 3.65 ug per sample. On the basis of a 24 hour sampling period the corresponding detection limits would be 0.12, 0.29, 0.26, and 0.36 ug per cubic metre respectively. The detection limits for the 6 day sampling periods are a factor of six less. The detection limits for a 24 hour sampling period for the particulate  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ , were 0.07, 0.09, and 0.10 ug per cubic metre.

#### 5.2.2.3 Sampler Performance

The amounts of each ion collected on the annular denuder tubes 1 and 2, which were coated with  $\text{Na}_2\text{CO}_3$ , tube 3, which was coated with citric acid, and the Teflon and nylon filters (not blank corrected) are shown in Tables 4 and 5.

The mean amount of  $\text{SO}_2$  collected on the first annular denuder tube during a 24-hour sampling period, measured and reported as  $\text{SO}_4^{2-}$ , was 83.99 ug. This is well above the average amount of  $\text{SO}_4^{2-}$  contamination found on the denuder tubes, which averaged 0.95 ug. The mean amount of  $\text{SO}_4^{2-}$  on the second tube was 6.62 ug. Comparing the amounts on the two tubes, after subtraction of contamination, showed that 93.6 percent of the  $\text{SO}_2$  was collected by the first tube. This is in keeping with the theoretical efficiency of annular denuder tubes of these dimensions at an ambient air sampling rate of 7.0 litres per minute (Possanzini et al, 1983). The amounts of  $\text{HNO}_3$  collected on tubes 1 and 2 were considerably less, 5.65 and 2.47 ug per tube. The efficiency of the  $\text{Na}_2\text{CO}_3$  coated tubes in collecting  $\text{HNO}_3$  is lower than for  $\text{SO}_2$  with the first tube collecting 73.3 percent. The  $\text{Na}_2\text{CO}_3$  coated tubes collect a small portion of the  $\text{NO}_2$  as well as the  $\text{HNO}_2$  in the atmospheric sample. Tube 1 retained an average of 3.96 ug of nitrite ion and tube 2, 0.77 ug. Previous studies of the collection of ammonia gas on citric acid coated tubes have shown the efficiency to be close to 100 percent (Peake and Legge, 1989). The average amount of  $\text{NH}_3$ , reported as  $\text{NH}_4^+$ , collected on tube 3 was 26.44 ug.



Table 4. Amount of each ion collected on tubes and filters during a 24-hour sampling period, (micrograms per sample).

<u>Tubes</u>							
	T1NO <sub>2</sub> <sup>-</sup>	T1NO <sub>3</sub> <sup>-</sup>	T1SO <sub>4</sub> <sup>=</sup>	T2NO <sub>2</sub> <sup>-</sup>	T2NO <sub>3</sub> <sup>-</sup>	T2SO <sub>4</sub> <sup>=</sup>	T3NH <sub>4</sub> <sup>+</sup>
Mean	3.96	5.65	83.99	0.77	2.47	6.62	26.44
Number	9	9	9	9	9	9	9
Std.Dev	1.41	3.42	55.84	0.11	1.04	4.41	17.72
Maximum	6.72	10.20	159.44	0.89	4.07	14.94	53.86
Minimum	1.83	1.63	7.81	0.55	0.78	2.35	7.75

<u>Filters</u>									
	TeNO <sub>3</sub> <sup>-</sup>	TeSO <sub>4</sub> <sup>=</sup>	TeNH <sub>4</sub> <sup>+</sup>	NyNO <sub>3</sub> <sup>-</sup>	NySO <sub>4</sub> <sup>=</sup>	TeCa <sup>++</sup>	TeMg <sup>++</sup>	TeNa <sup>+</sup>	TeK <sup>+</sup>
Mean	11.13	5.48	10.40	2.36	0.62	0.98	0.09	0.97	1.01
Number	9	9	7	9	8	7	9	9	9
Std.Dev	12.70	6.97	11.98	1.73	0.17	1.30	0.05	0.51	0.69
Maximum	28.94	22.20	33.58	5.87	0.88	3.25	0.16	1.90	1.86
Minimum	0.21	0.58	0.89	0.29	0.41	0.02	0.02	0.24	0.08

Fine particles, which consisted largely of NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>, were collected on the Teflon filter. The average amounts of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup>, and NH<sub>4</sub><sup>+</sup> ions collected were 11.13, 5.48, 10.40 ug, respectively, well above the blank filter values of 0.24, 0.38, and 0.56. Fine particles of ammonium nitrate are easily volatilized from the Teflon filter and the resulting NO<sub>3</sub><sup>-</sup> is collected on the nylon filter. The mean amount of NO<sub>3</sub><sup>-</sup> collected by the nylon filter was 2.36 ug as compared with a blank nylon filter value of 0.38 ug. Fifteen percent of the NO<sub>3</sub><sup>-</sup> was lost from the Teflon filter.



Table 5. Amount of each ion collected on tubes and filters during a 6-day sampling period, (micrograms per sample).

<u>Tubes</u>							
	T1NO <sub>2</sub> <sup>-</sup>	T1NO <sub>3</sub> <sup>-</sup>	T1SO <sub>4</sub> <sup>=</sup>	T2NO <sub>2</sub> <sup>-</sup>	T2NO <sub>3</sub> <sup>-</sup>	T2SO <sub>4</sub> <sup>=</sup>	T3NH <sub>4</sub> <sup>+</sup>
Mean	14.7	40.0	519.0	2.4	8.28	18.7	107.2
Number	13	13	13	12	12	12	13
Std.Dev	9.21	15.5	204.8	1.47	2.86	6.17	78.8
Maximum	36.4	60.9	812.4	5.69	13.2	28.9	251.5
Minimum	5.1	13.5	173.0	0.67	4.41	7.91	10.9

<u>Filters</u>									
	TeNO <sub>3</sub> <sup>-</sup>	TeSO <sub>4</sub> <sup>=</sup>	TeNH <sub>4</sub> <sup>+</sup>	NyNO <sub>3</sub> <sup>-</sup>	NySO <sub>4</sub> <sup>=</sup>	TeCa <sup>++</sup>	TeMg <sup>++</sup>	TeNa <sup>+</sup>	TeK <sup>+</sup>
Mean	111.0	51.2	83.7	17.3	1.32798	1.39	0.21	1.91	2.24
Number	13	13	12	13	13	13	13	11	13
Std.Dev	105.6	31.6	51.8	10.6	0.79	1.54	0.14	1.23	0.90
Maximum	356.2	102.9	182.1	33.9	2.85	4.88	0.49	5.16	4.46
Minimum	4.70	4.74	12.3	0.66	0.23	0.02	0.01	0.28	0.78

The amounts of each ion collected using six day sampling periods are presented in Table 5. As would be expected, the average amounts were generally, but not always, about six times greater than those collected with 24 hours of sampling. After subtraction of blank values, the total of the SO<sub>4</sub><sup>=</sup> collected on tubes 1 and 2, was 535.8 ug with the six day sampling. This was 6.0 times the amount collected with 24-hour sampling. In the case of NO<sub>3</sub><sup>-</sup> collected on tubes 1 and 2 the total was 47.1 ug or 6.9 times the 24-hour sample. This may indicated some conversion of NO<sub>2</sub> to NO<sub>3</sub><sup>-</sup> on the sampling tubes over the 6-day period. For ammonia the corresponding values were 105.4 ug and 24.7 ug, a

factor of 4.3 times, indicating some loss of  $\text{NH}_3$  from the citric acid coated tubes over 6 days. Interestingly, the ratios of ions collected on filters was consistently higher than on tubes. The amount of  $\text{SO}_4^{2-}$  on the Teflon filter was 50.8 ug, a factor of 10.0 greater than with the 24-hour sampling period. The corresponding values for  $\text{NO}_3^-$  on the Teflon filter,  $\text{NH}_4^+$  on the Teflon filter, and  $\text{NO}_3^-$  on the nylon filter were: 110.8 ug and 10.2 times, 83.1 ug and 8.4 times, and 16.7 ug and 9.5 times. The cause of these higher ratios is unknown. The calcium, magnesium, sodium, and potassium analytical results were inconsistent and appeared to be unreliable.

### 5.3 Ambient Concentrations

The mean concentrations of gases and particles collected from the ambient atmosphere at Royal Park, with 24 hour and 6 day sampling periods, are shown in Table 6. Concentrations at Royal Park were higher than those measured during the ADRP study at Fortress Mountain. They were generally comparable to the concentrations measured at the ADRP Crossfield East and West sites.

The mean concentration of  $\text{SO}_2$  (reported as  $\text{SO}_4^{2-}$ ) was 8.98 ug per  $\text{m}^3$  for the 9 samples collected over 24 hour periods and 9.51 ug per  $\text{m}^3$  for the 13 six-day samples. The range was 0.93 to 16.35 ug per  $\text{m}^3$  with 24-hour sampling and 2.97 to 13.84 with the 6-day sampling. The mean values are the equivalent of 2.0 and 2.2 ppb  $\text{SO}_2$  in the atmosphere, and given a deposition velocity of 0.7 cm/s, would equate to dry deposition values of 20 kg/ha/y and 21 kg/ha/y as  $\text{SO}_4^{2-}$ .

The concentrations of  $\text{SO}_2$  measured at Royal Park were considerably greater than the mean of 2.0 ug per  $\text{m}^3$  found during the ADRP study at Fortress Mountain, and similar to the 6.6 and 8.4 ug per  $\text{m}^3$  measured at the Crossfield West and East sites (Table 7). Care must be taken, however, in comparing the limited data obtained at Royal Park over a few weeks in winter, with the two years of continuous data collected during the ADRP. Concentrations were lower than reported for a forested area of central Germany and in the San Gabriel Mountains of Southern California (U. Damngen, personal communication; Bytnerowicz and Miller, 1991). Nevertheless the data clearly indicate that Royal Park is under the influence of regional air pollution from a multitude of sources, large and small.

Table 6. Concentrations of pollutants in the ambient atmosphere at Royal Park, Alberta.

(micrograms per cubic metre)

	<u>Six day samples</u>					<u>Six day blanks</u>				
	Mean	"n"	Std Dev	Max.	Min.	Mean	"n"	Std Dev	Max.	Min.
SO <sub>2</sub> as SO <sub>4</sub> <sup>-</sup>	8.98	13	3.35	13.84	2.97	0.06	16	0.09	0.36	0.01
HNO <sub>2</sub>	0.22	13	0.15	0.61	0.07	0.00	16	0.01	0.02	-0.01
HNO <sub>3</sub>	0.78	13	0.29	1.18	0.27	0.02	16	0.01	0.06	0.00
NH <sub>3</sub>	1.71	13	1.26	3.88	0.13	0.03	16	0.04	0.16	0.00
Particulate SO <sub>4</sub> <sup>-</sup>	0.87	13	0.55	1.70	0.07	0.01	16	0.00	0.01	0.00
Particulate NO <sub>3</sub> <sup>-</sup>	2.22	13	1.99	7.26	0.21	0.01	16	0.01	0.02	0.00
Particulate NH <sub>4</sub> <sup>+</sup>	1.37	13	1.01	3.64	0.01	0.01	16	0.00	0.02	0.00
	<u>Twenty four hour samples</u>					<u>Twenty four hour blanks</u>				
	Mean	"n"	Std Dev	Max.	Min.	Mean	"n"	Std Dev	Max.	Min.
SO <sub>2</sub> as SO <sub>4</sub> <sup>-</sup>	9.51	9	5.66	16.35	0.93	0.35	16	0.54	2.14	0.05
HNO <sub>2</sub>	0.34	9	0.15	0.59	0.10	0.01	16	0.04	0.10	-0.06
HNO <sub>3</sub>	0.73	9	0.42	1.23	0.23	0.12	16	0.09	0.38	0.01
NH <sub>3</sub>	2.83	9	2.77	9.23	0.46	0.20	16	0.21	0.94	0.00
Particulate SO <sub>4</sub> <sup>-</sup>	0.52	9	0.69	2.17	0.02	0.04	16	0.02	0.08	0.01
Particulate NO <sub>3</sub> <sup>-</sup>	1.28	9	1.24	3.01	0.03	0.08	16	0.05	0.15	-0.01
Particulate NH <sub>4</sub> <sup>+</sup>	0.83	8	1.14	3.19	-0.13	0.07	15	0.03	0.10	-0.01

Table 7. Concentrations of atmospheric pollutants at ADP, ADRP, and other sites.

	(micrograms per cubic metre)					
	<u>Gases</u>				<u>Particles</u>	
	SO <sub>2</sub>	HNO <sub>3</sub>	HNO <sub>2</sub>	NH <sub>3</sub>	SO <sub>4</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
Royal Park , 24-hour	9.51	0.73	0.34	2.83	0.52	1.28
Royal Park , 6 day	8.89	0.78	0.22	1.71	0.87	2.22
Fortress Mountain	2	0.31	0.05	0.26	0.43	0.03
Crossfield West	6.6	0.47	0.21	1.5	0.89	0.34
Crossfield East	8.5	0.51	0.38	2	0.96	0.42
Rotenkamp, Germany	14.3	1	1.2	3.7	8.8	4.9
Whittiker forest, Calif.	2.3	1.2		1.8		
Shirley Meadow, Calif.	2.2	2		2.3		
S. Sierra Nevada, Calif.	2.6	12.5		1.2		

Nitric acid concentrations were much lower than SO<sub>2</sub> concentrations, 0.73 ug per m<sup>3</sup> with 24-hour sampling and 0.78 ug per m<sup>3</sup> with 6-day sampling. Again these values were higher than the 0.31 ug per m<sup>3</sup> measured at Fortress Mountain, and were greater than the 0.47 and 0.51 ug per m<sup>3</sup> measured at Crossfield West and East. Concentrations were similar to those in central Germany but much lower than encountered in Southern California. Similarly the mean HNO<sub>2</sub> concentrations of 0.34 and 0.22 ug per m<sup>3</sup> at Royal Park were close to those measured at the Crossfield sites and well above the 0.05 ug per m<sup>3</sup> found at Fortress Mountain, as were the ammonia concentrations. The mean 24-hour ammonia value was skewed by a maximum measured value of 9.23 , well above the mean. Such occasional elevated concentrations due to local agricultural emissions are to be expected.

Particulate SO<sub>4</sub><sup>-</sup> concentrations were similar to those of the Fortress sampling sites however the NO<sub>3</sub><sup>-</sup> concentrations were considerably higher at Royal Park. The mean



$\text{NO}_3^-$  concentration for the 24-hour sample periods was 1.28 ug per  $\text{m}^3$ , and for the 6-day sampling period was 2.22 ug per  $\text{m}^3$  as compared with 0.34 ug per  $\text{m}^3$  at Crossfield West and 0.42 ug per  $\text{m}^3$  at Crossfield East. If the high values at Royal Park are confirmed by sampling for at least one year, it is speculated that the elevated  $\text{NO}_3^-$  concentrations are due to emissions of  $\text{NO}_x$  from motor vehicles, industry, and coal fired power plants in areas to the west.

## 6.0 EFFECTIVE ACIDITY

The effective acidity concept is one approach which may be used to set acidic deposition limits for Alberta. "Effective acidity" (EA) is a method of estimating the degree of acidification, in strong acid equivalents, which a soil would experience as a result of atmospheric inputs. The concept was applied by Coote et al (1981) who proposed that soil acidification in Eastern Canada could best be estimated by the equation:

$$\text{Eq}(1) \quad \text{EA} = ([\text{H}^+] + 1.15 \times [\text{NH}_4^+] - 0.7 \times [\text{NO}_3^-])$$

with the amounts of  $\text{H}^+$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  measured as wet deposition. The Management Committee of the Acid Deposition Program raised questions as to whether the factors in equation 1, which were developed for agricultural soils in Ontario are applicable to the Alberta situation. These, together with questions regarding the influence on effective acidity of the dry deposition of gases other than  $\text{SO}_2$ , such as  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{NO}_2$ , and the wet and dry deposition of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ , were discussed with a number of scientists in Alberta.

To further scientific discussion, the relative importance of the various chemical species in the calculation of effective acidity was evaluated using wet and dry deposition data from three Alberta locations. Effective acidity was calculated using a simple wet deposition equation (Eq 1), and the equation of Singleton et al (1988) which includes dry  $\text{SO}_4^{--}$  and  $\text{SO}_2$  deposition. EA was also calculated with four modifications of the Singleton equation. Furthermore, the net acidifying potential (NEP), as defined by Brydges and Summers (1989) was also calculated. The results are contained in the accompanying



report entitled "A comparison of methods for calculating effective acidity (EA) based on Alberta data". The conclusions and recommendations from that report were:

1. Dry deposition of sulphur dioxide and gaseous ammonia dominate the effective acidity values calculated for those areas of the province where natural gas processing and agriculture are major industries.

2. Wet deposition of  $\text{NH}_4^+$  has a greater influence on the calculated effective acidity than does wet  $\text{H}^+$  deposition in agricultural areas and is of roughly equivalent importance in areas remote from emission sources.

3. Wet deposition of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  should not be included as a specific term in the effective acidity calculation as their neutralizing effect is already accounted for in the  $\text{H}^+$  measurement.

4. Coarse particle  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  deposition should not be included as a specific term in the effective acidity calculation as they are part of the soil system effected by acid deposition rather than being a contributor to the process.

5. Effective acidity values are greatly influenced by the factors used in the equation to describe the chemistry of nitrogen in soils. The chemistry in Alberta soils of  $\text{NH}_3$  gas after deposition and of wet  $\text{NH}_4^+$  deposition, needs to be examined from a theoretical perspective and with the use of existing soils data. (Studies of acidification caused by the use of anhydrous ammonia as a fertilizer may be of value.)

6. Effective acidity values are also greatly influenced by the amount of  $\text{NO}_3^-$  leaching which occurs. The question of how to calculate the amount of  $\text{NO}_3^-$  leaching under the varying soil and climatic conditions found in Alberta needs to be addressed before effective acidity can become a useful tool in environmental management. It is recognized that existing information is limited but nevertheless some estimates need to be made to provide a range of values for use in the EA calculation.

Further discussions were held during the ADP Effective Acidity Workshop held February 20, 1992. At the workshop, the need to evaluate those factors which most contribute to effective acidity was expressed. In response, a computer program has been designed which takes into account twelve dependent and independent variables which affect the calculation of effective acidity when both wet and dry deposition are considered.

The program was used to produce illustrative tables of effective acidity with the ADRP data from Fortress Mountain and Crossfield East.

### 6.1 Methodology

The program for calculating effective acidity made use of "acidification factors" which describe the acidification of the soil resulting from the chemical reaction of one mole of deposited material in the soil. The equation is:

$$EA = a[\text{NH}_4^+] + b[\text{NO}_3^-] + c[\text{SO}_2] + d[\text{SO}_4^{2-}] + e[\text{NH}_3] + f[\text{HNO}_3] + g[\text{HNO}_3] + h[\text{NO}_2]$$

Acidification factors are designated "a,b,c...h", and [ ] indicates the amount of material deposited to the soil as wet or dry deposition. For wet deposition, the amount of deposition is a function of the amount of precipitation, D, and the concentration, C, of the ion in question. For dry deposition the [ ] is a function of the atmospheric concentration, C, and the deposition velocity, Vd for each gas or particulate species.

#### 6.1.1 Acidification factors

Each acidification factor is defined by a number of variables.

In the case of wet deposition of  $\text{NH}_4^+$  the acidification factor "a" is defined by the following:

(1) A percentage ( $\alpha$ ) of the wet  $\text{NH}_4^+$  deposition is volatilized, fixed in the soil, or taken up by plants.

(2) The remaining wet  $\text{NH}_4^+$  deposition ( $1-\alpha$ ) is nitrified.

(3) A percentage ( $\beta$ ) of the  $\text{NO}_3^-$ , derived from the nitrification of  $\text{NH}_4^+$ , is denitrified.

(4) A percentage ( $\gamma$ ) of the  $\text{NO}_3^-$ , derived from the nitrification of  $\text{NH}_4^+$ , is taken up by plants.

(5) A percentage ( $\delta$ ) of the  $\text{NO}_3^-$ , derived from the nitrification of  $\text{NH}_4^+$  (as well as  $\text{NO}_3^-$  from wet deposition), is leached from the soil.

In the case of wet deposition,  $\beta + \gamma + \delta$  must equal 100%.

Assumptions are made that each of the above processes produces or removes  $\text{H}^+$  by chemical reactions within the soil.

- (1) The first process, volatilization, fixation and direct plant uptake, is assumed to generate one  $H^+$  for each  $NH_4^+$  volatilized etc.
- (2) Process number two yields 2  $H^+$  for each  $NH_4^+$ .
- (3) Process number three removes one  $H^+$  for each  $NO_3^-$  denitrified.
- (4) Process number four removes one  $H^+$  for each  $NO_3^-$  taken up, and
- (5) One  $H^+$  is removed for each  $NO_3^-$  remaining in the soil.

For example: if  $\alpha = 50\%(0.5)$ ,  $\beta = 10\%$ , and  $\delta = 30\%$ , then  $\gamma = 60\%$  and the acidification factor "a" =  $(0.5 \times 1) + (1 - 0.5)(2) + (0.5 \times 0.1)(-1) + (0.5 \times 0.6)(-1)$

$$= 0.5 \quad + \quad 1.0 \quad -0.05 \quad -0.3$$

$$= 1.15$$

In the case of the wet deposition of  $NO_3^-$ , each  $NO_3^-$  remaining in the soil removes one  $H^+$  thus, in this example, the acidification factor "b" =  $(1 - 0.3)(-1) = -0.7$

The dry deposition of  $SO_2$  is assumed to have 2  $H^+$  associated with each  $SO_2$ , thus the acidification factor "c" = 2.0. Similarly, particulate  $SO_4^{2-}$  is assumed to exist as  $H_2SO_4$  and "d" = 2.0. It is assumed that upon deposition of  $NH_3$  gas to the soil, it would be converted to  $NH_4^+$  removing one  $H^+$ . The resulting  $NH_4^+$  would behave as wet  $NH_4^+$  deposition thus the acidification factor "e" would be "a" - 1. Similarly, it is assumed that upon deposition to the soil, gaseous  $HNO_3$ ,  $HNO$ , and  $NO_2(NO_x)$  would be converted to  $NO_3^-$  releasing one  $H^+$ , thus the acidification factors "f", "g", and "h" are equal to  $1 + "b"$ .

#### 6.1.2 Deposition velocity

The amount of dry deposition is a function of the atmospheric concentration of each species "C" and deposition velocity "Vd" of each gas or particle size fraction. Vd is a function of the resistances to deposition  $R_a$ ,  $R_b$ , and  $R_c$  which are controlled by the meteorology, surface properties of the landscape, and chemical and physical properties of the gas or particle. In this study, ranges of deposition velocities used to calculate dry deposition, producing ranges of EA values. Further work is required to determine deposition velocities most appropriate for each area of the province and season of the year.



## 6.2 Results and Discussion

By using the computer program with ranges for each of the variables, tables of EA have been created using the ADRP data. Evaluation of these results is proceeding to produce a sensitivity analysis for effective acidity. In view of the importance of setting target loading values in Alberta within the next few months this work is of high priority and it is anticipated that it will continue during the 1992-1993 fiscal year.

## 7.0 DEPOSITION VELOCITY

As described in the introduction and effective acidity parts of this report, sections 2.0 and 6.0, and illustrated in Figure 1, the determination of deposition velocities appropriate for each area of the province and for each season of the year is key to measuring dry deposition and its environmental effects. Furthermore these estimates are key to predicting spacial and temporal distribution patterns by the use of computer models. It follows that deposition velocity estimates are also key in establishing target loadings, or deposition limits, in the province.

As discussed earlier, the inferential method, proposed by Hicks et al (1987), offers a means of estimating dry deposition based on the atmospheric concentrations of pollutants and their deposition velocities. The inferential approach to estimating deposition velocity is based upon an analogy to an electrical circuit with:

$$V_d = \frac{1}{R_a + R_b + R_c}$$

The resistance to deposition is divided into three components; the aerodynamic resistance,  $R_a$ ; the boundary layer resistance,  $R_b$ ; and the canopy resistance (or surface resistance),  $R_c$ . Approximate values for  $R_a$  and  $R_b$  can be calculated from meteorological measurements of the wind profile, and the standard deviation in wind direction (Hicks et al, 1987). Because these parameters are influenced by atmospheric stability, measurements of temperature and wind profile to a height of at least 10m are required.

The surface resistance,  $R_c$ , often dominates the deposition velocity calculation. It is generally inferred rather than measured and can vary greatly; from zero for a wet or

alkaline surface to  $1000 \text{ s cm}^{-1}$  for smooth, snow covered surfaces. Because  $R_c$  is a function of the condition of the surface it can change rapidly, depending, in part, on whether the surface is wet or dry. For vegetated surfaces,  $R_c$  depends upon the stomatal resistance and the leaf mesophyll resistance which are affected by humidity, temperature, and solar radiation. As a result  $R_c$  and  $V_d$  show strong diurnal variations. Estimates of  $R_c$  require observations of the degree to which the land within about one km of the measurement site is covered with vegetation, agricultural soil, or lakes, as well as the surface wetness and the degree of plant activity (Figure 1).

Although  $R_c$  may be dominant under some conditions, the resistances controlled by meteorology,  $R_a$  and  $R_b$ , may be dominant in others. Wesely and Hicks (1977) proposed that  $R_a$  could be calculated as  $(1/k u_*) [\ln(z/z_o) - \psi_d]$ . A simplified method of calculating  $R_a$  based upon the wind speed,  $u$ , and the standard deviation in wind direction over 15 minutes,  $\sigma$ , is used by Hicks. Under stable conditions the equation for  $\text{SO}_2$  and  $\text{HNO}_3$  can be simplified to  $R_a = 4/(u \times \sigma^2)$ , or for unstable conditions  $R_a = 9/(\mu \times \sigma^2)$ . Following the same reasoning  $R_b$  can be calculated as,  $R_b = 7.225/(\mu \times R_a)^{1/2}$ . Hicks used the criteria for stability as a  $\sigma$  of less than  $10^\circ$  and positive solar radiation. The assumptions made by Hicks may cause major errors in the calculations of  $R_a$  and  $R_b$ . Efforts are being made to refine the calculations and to compare the results using several methods. Randy Angle and Dave Slubic have considered some of the alternatives.

In the equation of Wesely and Hicks,  $k$ , von Karmann's constant, and  $z$ , the reference height, are known leaving the variables:  $u_*$ , the friction velocity;  $z_o$ , the roughness length; and  $\psi_c$ , a correction factor to be determined. For  $\text{SO}_2$  the correction factor for the gas is the same as for heat transfer thus  $\psi_c = \psi_h$ . For neutral conditions  $\psi_h = 0$ ; for stable conditions  $\psi_h = -5z/L$ ; and for unstable conditions  $\psi_h = 2 \ln[(1 + x^2)/2]$  where  $x = (1 - 15z/L)^{1/4}$ , and  $L$  = the Monin Obukhov length.

Stability may be better defined on the basis of temperature gradient rather than the standard deviation in wind direction. The towers at the monitoring sites are equipped to measure the temperature difference between 2m and 10m. From the dry adiabatic lapse rate, stable conditions exist if  $\Delta T$  is less than  $0.078^\circ\text{C}$  and unstable conditions exist if  $\Delta T$  is greater than this value. In practice the instruments available cannot measure  $\Delta T$  with



sufficient accuracy and any measureable value of  $\Delta T > 0.1$  may be considered unstable. This approach was used in calculations of deposition velocity during the ADRP.

Once the stability has been determined it is possible to calculate  $z_0$ ,  $u_*$ , and  $L$  using a series of equations based on three different approaches: (1) the turbulence method (2) the method of Walcek et al (1986); and net radiation methods.

Testing of the different approaches to calculating  $R_a$  and  $R_b$  and application of the inferential method of calculating deposition velocity requires the following measurements: (1) temperature at 10m, (2) difference in temperature between 10m and 2m, (3) Wind speed at 10m and 2m, (4) standard deviation in wind direction, 15 minute, (5) vertical wind speed, (6) photosynthetic radiation, (7) humidity, and (8) surface wetness. Not all measurements will be required once the most appropriate methods for determining  $R_a$  and  $R_b$  are established. Observational data is also necessary: (1) the presence of snow cover, (2) the percentage of the area within 1 km of the site which is covered by vegetation or water or is cultivated, (3) the stage of crop development and amount of the cultivated soil visible, (4) evidence of drought or environmental stress, and, (5) any other observations pertaining to the physical, chemical, and biological properties of the land surface. These measurements and observations are required for site specific estimates of deposition velocities. On a broader, regional scale, aerial photography and satellite imagery may be used to make estimates on an 80km grid.

A simple computer program has been written to calculate  $R_a$  and  $R_b$  based on the approach of Wesely and Hicks (1977) and has been applied to selected data from the ADRP. Similar programs will be written for other methods of calculating  $R_a$  and  $R_b$ , the methods will be compared, and recommendations made as to the most appropriate method to be used in the Alberta dry deposition monitoring network.

## 8.0 DATA BASE

The EQMB, through a contract with the Coopers and Lybrand Consulting Group, is designing a data base which will accept data from the ADP and integrate it with existing data bases resulting in a comprehensive data base for all Alberta air quality monitoring data. One aspect of the Technology Evaluation Project is to ensure that the needs of the

ADP dry deposition monitoring network are properly served by the new data base and to ensure that data produced by the network is in a format compatible with the new data base. To these ends, the ARC has participated in meetings of the Data Management Working Committee along with members of the EQMB, AEC, and the consultants. The outputs from the chemical analysis of the dry deposition monitoring samples are recorded on spreadsheets which calculate ambient concentrations of pollutants in a format which is compatible with the new data base.

Existing wet and dry deposition data has been reformatted so that it may be integrated, without further conversion, into the new data base. The data will be provided to the EQMB on disks, in Excel, which is compatible with most data bases.

## 9.0 REFERENCES

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## **A P P E N D I X 1.**

### **Project Management Plan**





Acid Deposition Program,  
Technology Evaluation and  
initial Monitoring program.

Project: 2JULY

Date: Mar 10, 1992 2:28 PM

1	Select suitable sampling site	30.00 Days
	Sched Start: Nov 1, 1990 8:00 AM	Sched Finish: Dec 12, 1990 5:00 PM
2	Obtain sampling and met. towers	20.00 Days
	Sched Start: Nov 1, 1990 8:00 AM	Sched Finish: Nov 28, 1990 5:00 PM
3	Define data base parameters	60.00 Days
	Sched Start: Nov 15, 1990 8:00 AM	Sched Finish: Feb 15, 1991 5:00 PM
4	Select monitoring equipment	45.00 Days
	Sched Start: Nov 15, 1990 8:00 AM	Sched Finish: Jan 25, 1991 5:00 PM
5	Ship tower equipment to Vegreville	10.00 Days
	Sched Start: Nov 29, 1990 8:00 AM	Sched Finish: Dec 12, 1990 5:00 PM
6	Establish sampling schedule	100.00 Days
	Sched Start: Dec 3, 1990 8:00 AM	Sched Finish: May 2, 1991 5:00 PM
7	Establish sampling protocol	100.00 Days
	Sched Start: Dec 3, 1990 8:00 AM	Sched Finish: May 2, 1991 5:00 PM
8	Find AD flow control system	10.00 Days
	Sched Start: Dec 3, 1990 8:00 AM	Sched Finish: Dec 14, 1990 5:00 PM
9	Install sampling and met. towers	30.00 Days
	Sched Start: Dec 13, 1990 8:00 AM	Sched Finish: Feb 1, 1991 5:00 PM
10	Lease sampling site	20.00 Days
	Sched Start: Dec 13, 1990 8:00 AM	Sched Finish: Jan 18, 1991 5:00 PM
11	Obtain annular denuder controller	20.00 Days
	Sched Start: Jan 15, 1991 8:00 AM	Sched Finish: Feb 11, 1991 5:00 PM
12	Obtain annular denuder pumping system	20.00 Days
	Sched Start: Jan 15, 1991 8:00 AM	Sched Finish: Feb 11, 1991 5:00 PM
13	Obtain trolleys for towers	20.00 Days
	Sched Start: Jan 21, 1991 8:00 AM	Sched Finish: Feb 15, 1991 5:00 PM
14	Select analytical laboratory	1.00 Day
	Sched Start: Mar 7, 1991 8:00 AM	Sched Finish: Mar 7, 1991 5:00 PM

15 Obtain 1991-1992 funding	1.00 Day
Sched Start: Apr 1, 1991 8:00 AM	Sched Finish: Apr 1, 1991 5:00 PM
16 Establish wet anal QA/QC procedures	20.00 Days
Sched Start: Apr 15, 1991 8:00 AM	Sched Finish: May 10, 1991 5:00 PM
17 Establish dry anal QA/QC procedures	20.00 Days
Sched Start: Apr 15, 1991 8:00 AM	Sched Finish: May 10, 1991 5:00 PM
18 Establish field QA/QC procedures	20.00 Days
Sched Start: Apr 15, 1991 8:00 AM	Sched Finish: May 10, 1991 5:00 PM
19 Establish dry dep analytical protocol	20.00 Days
Sched Start: Apr 15, 1991 8:00 AM	Sched Finish: May 10, 1991 5:00 PM
20 Order passive samplers	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
21 Order ozone analyzer	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
22 Order Sun computer	5.00 Days
Sched Start: Apr 24, 1991 8:00 AM	Sched Finish: Apr 30, 1991 5:00 PM
23 Order Monitoring Branch CAPMoN	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
24 Order annular denuder parts	5.00 Days
Sched Start: Apr 24, 1991 8:00 AM	Sched Finish: Apr 30, 1991 5:00 PM
25 Order Technology Evaluation CAPMoN	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
26 Order data base for Sun	5.00 Days
Sched Start: Apr 24, 1991 8:00 AM	Sched Finish: Apr 30, 1991 5:00 PM
27 Order meteorological equipment	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
28 Order precipitation sampler	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
29 Order analytical micro-balance	5.00 Days
Sched Start: Jul 2, 1991 8:00 AM	Sched Finish: Jul 8, 1991 5:00 PM
30 Order data logger	5.00 Days
Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM

31	Order CAPMoN filters	5.00 Days
	Sched Start: Jun 10, 1991 8:00 AM	Sched Finish: Jun 14, 1991 5:00 PM
32	Delivery of sampling and met. equipment	30.00 Days
	Sched Start: Jun 17, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
33	Find laboratory technician	20.00 Days
	Sched Start: Jun 24, 1991 8:00 AM	Sched Finish: Jul 22, 1991 5:00 PM
34	Delivery of Sun computer system	30.00 Days
	Sched Start: May 1, 1991 8:00 AM	Sched Finish: Jun 12, 1991 5:00 PM
35	Delivery of analytical micro-balance	15.00 Days
	Sched Start: Jul 9, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
36	Delivery of CAPMoN and AD filters	30.00 Days
	Sched Start: Jun 17, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
37	Delivery of data base for Sun	30.00 Days
	Sched Start: May 1, 1991 8:00 AM	Sched Finish: Jun 12, 1991 5:00 PM
38	Rebuild AD flow control system	5.00 Days
	Sched Start: Jul 9, 1991 8:00 AM	Sched Finish: Jul 15, 1991 5:00 PM
39	Obtain sampling inlet system	10.00 Days
	Sched Start: Jul 11, 1991 8:00 AM	Sched Finish: Jul 24, 1991 5:00 PM
40	Find trailer suitable for monitoring	5.00 Days
	Sched Start: Jul 11, 1991 8:00 AM	Sched Finish: Jul 17, 1991 5:00 PM
41	Ship AD equipment to Vegreville	10.00 Days
	Sched Start: Jul 16, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
42	Determine dry dep. calculation method	30.00 Days
	Sched Start: Jul 17, 1991 8:00 AM	Sched Finish: Aug 28, 1991 5:00 PM
43	Prepare monitoring trailer	5.00 Days
	Sched Start: Jul 18, 1991 8:00 AM	Sched Finish: Jul 24, 1991 5:00 PM
44	Install site access	5.00 Days
	Sched Start: Jul 19, 1991 8:00 AM	Sched Finish: Jul 25, 1991 5:00 PM
45	Install trailer at sampling site	5.00 Days
	Sched Start: Jul 23, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
46	Hire laboratory technician	1.00 Day
	Sched Start: Jul 23, 1991 8:00 AM	Sched Finish: Jul 23, 1991 5:00 PM



47	Train laboratory technician	10.00 Days
	Sched Start: Jul 24, 1991 8:00 AM	Sched Finish: Aug 7, 1991 5:00 PM
48	Develop monthly report software	25.00 Days
	Sched Start: Jul 24, 1991 8:00 AM	Sched Finish: Aug 28, 1991 5:00 PM
49	Install sampling inlet in trailer	3.00 Days
	Sched Start: Jul 25, 1991 8:00 AM	Sched Finish: Jul 29, 1991 5:00 PM
50	Obtain PC statistical software	30.00 Days
	Sched Start: Jul 26, 1991 8:00 AM	Sched Finish: Sep 9, 1991 5:00 PM
51	Install power in trailer	5.00 Days
	Sched Start: Jul 30, 1991 8:00 AM	Sched Finish: Aug 6, 1991 5:00 PM
* 52	Install meteorological equipment	6.00 Days
	Sched Start: Jul 30, 1991 8:00 AM	Sched Finish: Aug 7, 1991 5:00 PM
* 53	Install monitoring equipment	6.00 Days
	Sched Start: Jul 30, 1991 8:00 AM	Sched Finish: Aug 7, 1991 5:00 PM
54	Install telephone in trailer	5.00 Days
	Sched Start: Jul 31, 1991 8:00 AM	Sched Finish: Aug 7, 1991 5:00 PM
55	Program data logger	5.00 Days
	Sched Start: Aug 2, 1991 8:00 AM	Sched Finish: Aug 9, 1991 5:00 PM
56	Install precipitation sampler	3.00 Days
	Sched Start: Aug 2, 1991 8:00 AM	Sched Finish: Aug 7, 1991 5:00 PM
57	Install data logger in trailer	6.00 Days
	Sched Start: Aug 6, 1991 8:00 AM	Sched Finish: Aug 13, 1991 5:00 PM
58	PC-data logger communications	5.00 Days
	Sched Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
59	Sun-data logger communications	5.00 Days
	Sched Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
60	Set up micro balance in cabinet	5.00 Days
	Sched Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
* 61	Link equipment to data logger	4.00 Days
	Sched Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 13, 1991 5:00 PM
* 62	Calibrate and test equipment	5.00 Days
	Sched Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM

63	Set up AD tube drying train	5.00 Days
Sched	Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
64	Set up filter conditioning cabinet	5.00 Days
Sched	Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
65	Set up annular denuder prep system	5.00 Days
Sched	Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
66	Check laboratory instrumentation	5.00 Days
Sched	Start: Aug 8, 1991 8:00 AM	Sched Finish: Aug 14, 1991 5:00 PM
67	Determine dep. vel. calculation method	10.00 Days
Sched	Start: Aug 15, 1991 8:00 AM	Sched Finish: Aug 28, 1991 5:00 PM
68	Install Sun data base	5.00 Days
Sched	Start: Aug 15, 1991 8:00 AM	Sched Finish: Aug 21, 1991 5:00 PM
69	Prepare annular denuder systems	100.00 Days
Sched	Start: Aug 15, 1991 8:00 AM	Sched Finish: Jan 10, 1992 5:00 PM
70	Ship annular denuder units to site	100.00 Days
Sched	Start: Aug 16, 1991 8:00 AM	Sched Finish: Jan 13, 1992 5:00 PM
71	Install annular denuder units	100.00 Days
Sched	Start: Aug 22, 1991 8:00 AM	Sched Finish: Jan 17, 1992 5:00 PM
72	Install CAPMoN filter units	100.00 Days
Sched	Start: Aug 22, 1991 8:00 AM	Sched Finish: Jan 17, 1992 5:00 PM
73	Collect annular denuder samples	100.00 Days
Sched	Start: Aug 23, 1991 8:00 AM	Sched Finish: Jan 20, 1992 5:00 PM
74	Collect CAPMoN filter samples	100.00 Days
Sched	Start: Aug 23, 1991 8:00 AM	Sched Finish: Jan 20, 1992 5:00 PM
75	Install passive samplers	100.00 Days
Sched	Start: Aug 27, 1991 8:00 AM	Sched Finish: Jan 22, 1992 5:00 PM
76	Ship tubes and filters to laboratory	100.00 Days
Sched	Start: Aug 28, 1991 8:00 AM	Sched Finish: Jan 23, 1992 5:00 PM
77	Collect precipitation samples	100.00 Days
Sched	Start: Aug 28, 1991 8:00 AM	Sched Finish: Jan 23, 1992 5:00 PM
78	Transfer tube/filter analysis to PC	100.00 Days
Sched	Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM



* 79	QA/QC tube/filter analytical data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
80	Transfer sampler flow data to PC	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
81	QA/QA sampler flow data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
82	Collect meteorological data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
83	QA/QC meteorological data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
84	Transfer met. data to Sun and PC	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
85	Acquire sampling flow data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
86	Analyze precipitation samples	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
87	QA/QC precipitation analytical data	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
88	Transfer pptn analysis to Sun	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
* 89	Analyze tubes and filters	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
90	Analyze passive samplers	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
91	Calculate deposition velocity	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
* 92	Calculate dry deposition	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
* 93	Calculate wet deposition	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
* 94	Transfer all data to Sun data base	100.00 Days
	Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM

95 Calculate atmospheric concentrations	100.00 Days
Sched Start: Aug 29, 1991 8:00 AM	Sched Finish: Jan 24, 1992 5:00 PM
96 Statistical analysis on PC	98.00 Days
Sched Start: Sep 10, 1991 8:00 AM	Sched Finish: Jan 31, 1992 5:00 PM
97 Evaluation of laboratory protocol	95.00 Days
Sched Start: Sep 20, 1991 8:00 AM	Sched Finish: Feb 7, 1992 5:00 PM
98 Evaluation of sampler performance	95.00 Days
Sched Start: Sep 20, 1991 8:00 AM	Sched Finish: Feb 7, 1992 5:00 PM
99 Evaluation of sampling protocol	95.00 Days
Sched Start: Sep 20, 1991 8:00 AM	Sched Finish: Feb 7, 1992 5:00 PM
100 Produce monthly data reports	70.00 Days
Sched Start: Oct 21, 1991 8:00 AM	Sched Finish: Jan 31, 1992 5:00 PM
101 Network equipment recommendations	25.00 Days
Sched Start: Jan 13, 1992 8:00 AM	Sched Finish: Feb 14, 1992 5:00 PM
102 Methodology recommendations	25.00 Days
Sched Start: Jan 13, 1992 8:00 AM	Sched Finish: Feb 14, 1992 5:00 PM
103 Submit draft Tech. Eval. report	15.00 Days
Sched Start: Jan 29, 1992 8:00 AM	Sched Finish: Feb 19, 1992 5:00 PM
104 Review final report	10.00 Days
Sched Start: Feb 20, 1992 8:00 AM	Sched Finish: Mar 4, 1992 5:00 PM
105 Final report	10.00 Days
Sched Start: Mar 5, 1992 8:00 AM	Sched Finish: Mar 18, 1992 5:00 PM



Acid Deposition Program,  
Technology Evaluation and  
initial Monitoring program.

		1991						
		Nov	Dec	Jan	Feb	Mar	Apr	May
		-----+-----+-----+-----+-----+-----+-----						
1	Select suitable sampling site	O++++>						
2	Obtain sampling and met. towers	O+++>						
3	Define data base parameters	O+++++ +++++>						
4	Select monitoring equipment	O+++++ +++>						
5	Ship tower equipment to Vegreville	+ >+>			+	+	+	+
6	Establish sampling schedule	O++ ++++++>						
7	Establish sampling protocol	O++ ++++++>						
8	Find AD flow control system	O>						
9	Install sampling and met. towers	>+ +++++>						
10	Lease sampling site	+ >+ ++>				+	+	+
11	Obtain annular denuder controller			O+++>				
12	Obtain annular denuder pumping system			O+++>				
13	Obtain trolleys for towers			O+++>				
14	Select analytical laboratory					O		
15	Obtain 1991-1992 funding	+ +		+ +			O +	
16	Establish wet anal QA/QC procedures						O++>	
17	Establish dry anal QA/QC procedures						O++>	
18	Establish field QA/QC procedures						O++>	
19	Establish dry dep analytical protocol						O++>	
20	Order passive samplers	+ +		+ +		+	+	
21	Order ozone analyzer							
22	Order Sun computer						>>	
23	Order Monitoring Branch CAPMoN						>>	
24	Order annular denuder parts						>>	
25	Order Technology Evaluation CAPMoN	+ +		+ +		+	+	+
26	Order data base for Sun						>>	
27	Order meteorological equipment							
28	Order precipitation sampler							
29	Order analytical micro-balance							
30	Order data logger	+ +		+ +		+	+	+
31	Order CAPMoN filters							
32	Delivery of sampling and met. equipment							
33	Find laboratory technician							
34	Delivery of Sun computer system						>++++	
35	Delivery of analytical micro-balance	+ +		+ +		+	+	
36	Delivery of CAPMoN and AD filters							
37	Delivery of data base for Sun						>++++	
38	Rebuild AD flow control system							
39	Obtain sampling inlet system							
40	Find trailer suitable for monitoring	+ +		+ +		+	+	+
41	Ship AD equipment to Vegreville							
42	Determine dry dep. calculation method							
43	Prepare monitoring trailer							
44	Install site access							
45	Install trailer at sampling site	+ +		+ +		+	+	+
46	Hire laboratory technician							

[illegible]



Acid Deposition Program,  
Technology Evaluation and  
initial Monitoring program.

		1991						
		Nov	Dec	Jan	Feb	Mar	Apr	May
		+	+	+	+	+	+	+
47	Train laboratory technician							
48	Develop monthly report software							
49	Install sampling inlet in trailer							
50	Obtain PC statistical software							
51	Install power in trailer	+	+	+	+	+	+	+
52	Install meteorological equipment							
53	Install monitoring equipment							
54	Install telephone in trailer							
55	Program data logger							
56	Install precipitation sampler	+	+	+	+	+	+	+
57	Install data logger in trailer							
58	PC-data logger communications							
59	Sun-data logger communications							
60	Set up micro balance in cabinet							
61	Link equipment to data logger	+	+	+	+	+	+	+
62	Calibrate and test equipment							
63	Set up AD tube drying train							
64	Set up filter conditioning cabinet							
65	Set up annular denuder prep system							
66	Check laboratory instrumentation	+	+	+	+	+	+	+
67	Determine dep. vel. calculation method							
68	Install Sun data base							
69	Prepare annular denuder systems							
70	Ship annular denuder units to site							
71	Install annular denuder units	+	+	+	+	+	+	+
72	Install CAPMoN filter units							
73	Collect annular denuder samples							
74	Collect CAPMoN filter samples							
75	Install passive samplers							
76	Ship tubes and filters to laboratory	+	+	+	+	+	+	+
77	Collect precipitation samples							
78	Transfer tube/filter analysis to PC							
79	QA/QC tube/filter analytical data							
80	Transfer sampler flow data to PC							
81	QA/QA sampler flow data	+	+	+	+	+	+	+
82	Collect meteorological data							
83	QA/QC meteorological data							
84	Transfer met. data to Sun and PC							
85	Acquire sampling flow data							
86	Analyze precipitation samples	+	+	+	+	+	+	+
87	QA/QC precipitation analytical data							
88	Transfer pptn analysis to Sun							
89	Analyze tubes and filters							
90	Analyze passive samplers							
91	Calculate deposition velocity	+	+	+	+	+	+	+
92	Calculate dry deposition							

[illegible]

[illegible]

## 1991

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## SECTION 6

A Comparison of Methods for  
Calculating Effective Acidity (EA)  
Based on Alberta Data



**A Comparison of Methods for  
Calculating Effective Acidity (EA)  
Based on Alberta Data**

Prepared for the Management Committee  
of the Acid Deposition Program

Eric Peake

Environmental Research & Engineering Department  
Alberta Research Council

Revised: February, 1992





## A COMPARISON OF METHODS FOR CALCULATING EFFECTIVE ACIDITY (EA) BASED ON ALBERTA DATA.

Eric Peake, February, 1992

### INTRODUCTION

"Effective acidity" (EA) is a method of estimating the degree of acidification, in strong acid equivalents, which a soil would experience as a result of atmospheric inputs. It is one approach being considered for setting acidic deposition limits in Alberta (Alberta Environment, 1990).

The concept was applied by Coote et al (1981) who proposed that soil acidification in Eastern Canada could best be estimated by the equation:

$$(Eq\ 1) \quad EA = ([H^+] + 1.15 \times [NH_4^+] - 0.7 \times [NO_3^-])$$

with the amounts of  $H^+$ ,  $NH_4^+$ , and  $NO_3^-$  measured as wet deposition. The Management Committee of the Acid Deposition Program raised the question as to whether the factors in equation 1, which were developed for agricultural soils in Ontario are applicable to the Alberta situation. This question, together with questions regarding the influence of the dry deposition of gases other than  $SO_2$ , such as  $NH_3$ ,  $HNO_3$ ,  $HNO_2$ , and  $NO_2$ , and the wet and dry deposition of  $Ca^{++}$  and  $Mg^{++}$  were also raised and were discussed with a number of scientists in Alberta. Their responses are contained in this report.

To further the scientific discussions, the relative importance of the various chemical species in the calculation of effective acidity was evaluated using wet and dry deposition data from three Alberta locations. Effective acidity was calculated using a simple wet deposition equation (Eq 1), and the equation of Singleton et al (1988) which includes dry  $SO_4^{--}$  and  $SO_2$  deposition. EA was also calculated with four modifications of the Singleton equation. Furthermore, the net acidifying potential (NAP), as defined by Brydges and Summers (1989) was also calculated.

### BACKGROUND

Coote et al (1981) proposed that acidification of agricultural soils in Eastern Canada could best be estimated by the equation:

$$(Eq\ 1) \quad EA = ([H^+] + 1.15 \times [NH_4^+] - 0.7 \times [NO_3^-])$$

with the amounts of  $H^+$ ,  $NH_4^+$ , and  $NO_3^-$  measured as wet deposition. The  $[H^+]$  term is the direct contribution of the  $H^+$  as wet deposition whereas the  $1.15 \times [NH_4^+] - 0.7 \times [NO_3^-]$  term is the estimated effect of wet  $NH_4^+$  and  $NO_3^-$  deposition in generating acidity in the soil. The factors of 1.15 and -0.7 reflect the net effect of the nitrification, denitrification, fixation, plant uptake, and leaching processes in the soil which produce or remove  $H^+$ . Complete nitrification of  $NH_4^+$  by bacteria in soils generates 2  $H^+$  from each  $NH_4^+$  however when  $NH_4^+$  is taken up directly by plants only a single  $H^+$  is released. Nitrate, from wet deposition and

from nitrification of  $\text{NH}_4^+$ , is partially leached from the soil, denitrified, and taken up by plant roots. Direct uptake of  $\text{NO}_3^-$  by plants results in the release of an equivalent amount of  $\text{OH}^-$  thus neutralizing an equivalent amount of  $\text{H}^+$ .

To make a estimate of the contribution of atmospheric  $\text{NH}_4^+$  and  $\text{NO}_3^-$  to soil acidity it was necessary for Coote et al (1981) to make some assumptions about the extent of nitrification, denitrification, and leaching. Values cited from the literature gave values of from 2 to 60 percent for the nitrification of  $\text{NH}_4^+$ ; leaching rates of 2 to 31 percent of added N; and leaching plus gaseous losses of 0 to 69 percent (Russell, 1961). Other values cited were; 100 percent for nitrification of  $\text{NH}_4^+$  (Brady, 1974) and, combined leaching and denitrification losses in southern Ontario of from 0 to 48 percent of the total nitrogen (Cameron et al, 1977).

The assumptions made by Coote et al (1981) were:

- (i) that 50 percent of the  $\text{NH}_4^+$  was volatilized, fixed, or taken up directly by plants resulting in the generation of 0.5 equivalents of  $\text{H}^+$  per  $\text{NH}_4^+$ .
- (ii) that the remaining 50 percent of the  $\text{NH}_4^+$  was nitrified resulting in the generation of 1.0 equivalents of  $\text{H}^+$ .
- (iii) that 19 percent of the  $\text{NO}_3^-$  generated from the nitrification of  $\text{NH}_4^+$  was denitrified resulting in the uptake of 0.05 equivalents of  $\text{H}^+$ , and
- (iv) that 60 percent of the generated  $\text{NO}_3^-$  was taken up by plants resulting in the uptake of 0.3 equivalents of  $\text{H}^+$ .
- (v) that the remaining 30 percent of the generated  $\text{NO}_3^-$  was removed by leaching. This assumption applies to both  $\text{NO}_3^-$  generated from  $\text{NH}_4^+$  and  $\text{NO}_3^-$  deposited directly in precipitation.

As a result, each mole of  $\text{NH}_4^+$  would generate:

$$0.5 + 1.0 - 0.05 - 0.3 = 1.15 \text{ moles of } \text{H}^+.$$

In the case of the wet deposition of  $\text{NO}_3^-$ , 30 percent would be lost by leaching, thus each mole of  $\text{NO}_3^-$  deposited would reduce the  $\text{H}^+$  concentration in the soil by 0.7 moles.

It can readily be seen that the amount of nitrification, plant uptake, fixation, and leaching will greatly affect the acidification factors. For example, in the unlikely event that nitrification was close to 100 percent, as suggested by the data of Brady (1974), and that  $\text{NO}_3^-$  leaching was 70 percent, the upper range of data reported by Russell (1961), then each  $\text{NH}_4^+$  would generate 1.7  $\text{H}^+$  and each  $\text{NO}_3^-$  deposited would remove only 0.3  $\text{H}^+$  from the soil.

The equation of Coote et al (1981) calculates only the effect of wet deposition with dry deposition considered to be 40 percent of wet deposition in eastern Canada. In Western Canada dry deposition is a more significant factor in acidification processes and a term was added by Turchenek and Abboud (1990) and Singleton et al (1988) to account for the dry deposition of  $\text{SO}_4^{2-}$  and  $\text{SO}_2$ :

$$(\text{Eq } 2) \quad \text{EA} = (\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-) + (\text{SO}_4^{2-} + \text{SO}_2)$$

It is assumed that  $\text{SO}_4^{2-}$  and  $\text{SO}_2$  each introduce two equivalents of  $\text{H}^+$  to the system.



In their consideration of the acidifying effect of dry  $\text{NH}_3$  deposition, Brydges and Summers (1989) concluded that the  $\text{NH}_3$  would be oxidized to  $\text{NH}_4^+$  in the atmosphere with an equivalent reduction in  $\text{H}^+$ . Subsequently, the  $\text{NH}_4^+$  would be taken up in vegetation releasing an equivalent amount of  $\text{H}^+$ , thus the net effect would be zero. In contrast Coote et al (1981) calculated that the acidifying effect of wet  $\text{NH}_4^+$  deposition in soil was 1.15  $\text{H}^+$  equivalents. The oxidation of  $\text{NH}_3$  in the atmosphere is separate from the chemistry of  $\text{NH}_3$  in the soil. Presumably,  $\text{NH}_3$  deposited directly as a gas to a soil would be oxidized to  $\text{NH}_4^+$  in the soil, resulting in the uptake of one equivalent of  $\text{H}^+$ . The  $\text{NH}_4^+$  would generate 1.15 equivalents of  $\text{H}^+$  resulting in a net increase in acidity of 0.15  $\text{H}^+$  equivalents for each equivalent of  $\text{NH}_3$  gas deposited.

Similar arguments can be made for the effects of  $\text{HNO}_3$  and  $\text{HNO}_2$  deposition, with the ability of  $\text{NO}_3^-$  to remove  $\text{H}^+$  from the soil reduced by the amount of  $\text{NO}_3^-$  leached from the system, estimated to be about 30% by Coote et al (1981), resulting in a conversion factor of -0.7. In the case of direct  $\text{NO}_x$  deposition to soils, one  $\text{H}^+$  equivalent would be released in the formation of  $\text{NO}_3^-$ , and 30% of the  $\text{NO}_3^-$  would be leached from the system resulting in a conversion factor of +0.3.

#### OPINIONS OF ALBERTA SCIENTISTS

When scientists were questioned regarding the effective acidity factors developed by Coote et al (1981) which describe the acidifying effect of  $\text{NH}_4^+$  deposition, the general response was that, in the absence of factors developed specifically for Alberta soils, the factors of Coote et al (1981) were a reasonable starting point. Several scientists stressed the need for studies to develop factors for Alberta soil and climatic conditions.

On the question of dry  $\text{NH}_3$ ,  $\text{HNO}_3$ , and  $\text{NO}_2$  deposition, the general response was that these are important in those areas of the province with major industrial and agricultural emissions (as indicated by the ADRP data). In areas remote from such development, concentrations of  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{NO}_2$  were thought to be too small to contribute much to effective acidity. There was uncertainty about what deposition velocities should be used for gases, particularly for  $\text{NH}_3$ , and what factors to apply in estimating the contribution of dry  $\text{NH}_3$ ,  $\text{HNO}_3$ , and  $\text{NO}_x$  deposition to effective acidity.

On the question of the inclusion of a wet  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  term in the effective acidity equation; scientists agreed that this term was not required as the neutralizing effect of these ions is already reflected in the  $\text{H}^+$  concentration measured in the wet deposition.

#### CALCULATIONS OF EFFECTIVE ACIDITY USING ADRP DATA

To further the scientific discussions, the relative importance of the various chemical species in the calculation of effective acidity was evaluated using wet and dry deposition data from three Alberta locations. Effective acidity was calculated using a simple wet deposition equation (Eq 1), and the equation of Singleton et al (1988) which includes dry  $\text{SO}_4^{--}$  and  $\text{SO}_2$  deposition. EA was also calculated with four modifications of the Singleton equation. Furthermore, the net acidifying potential (NAP), as defined by Brydges and Summers (1989) was also calculated.

The wet and dry deposition data were obtained from the atmospheric monitoring sites operated during the Acid Deposition Research Program. These were: Fortress Mountain, Crossfield East, and Crossfield West. Fortress Mountain was a remote site representative of air quality away from regional and local sources of pollution. Crossfield East was located 2.5 km in a predominantly downwind direction from a sour gas processing plant which was estimated to emit 42 tonnes per day of  $\text{SO}_2$  and 2 tonnes per day of  $\text{NO}_x$ . This site was also under the influence of several sour gas processing plants within a 50 km radius, a major highway, and the city of Calgary. Crossfield West was located 6 km in a predominantly upwind direction from the sour gas processing plant. Air quality was influenced by several major sour gas processing plants within a 50 km radius and the city of Calgary.

The equations used in the calculations and their characteristics were:

1. Calculation of effective acidity using the Coote et al (1981) equation.

(Wet deposition)

$$\text{(Eq 1) } EA = [H^+ + 1.15NH_4^+ - 0.7NO_3^-]$$

This equation (i) uses only wet deposition measurements ignoring any contribution from dry deposition, (ii) uses the factors of -0.7 and 1.15 to calculate  $H^+$  equivalents for  $NO_3^-$  and  $NH_4^+$ , respectively in soil systems as proposed by Coote et al (1981).

2. Calculation of EA using the Singleton equation.

Abboud and Turchenek (1990) used this equation to calculate EA in soils as part of the ADRP.

$$\text{(Eq 2) } EA = [H^+ + 1.15NH_4^+ - 0.7NO_3^-] + [SO_4^{2-} + SO_2]$$

This equation; (i) takes into account both wet and dry deposition, (ii) uses factors of -0.7 and 1.15 to convert wet deposition of  $NO_3^-$  and  $NH_4^+$  respectively to  $H^+$  equivalents in soils, (iii) considers only dry S deposition (not N), (iv) assumes that each mole of dry  $SO_4^{2-}$  or  $SO_2$  is associated with two moles of  $H^+$ , and (v) does not include either wet or dry  $Ca^{++}$  or  $Mg^{++}$  deposition.

3. Expansion of Equation 2 to include dry deposition of nitrogen species using Coote's factors.

(Wet deposition)

(Dry deposition)

$$\text{(Eq 3) } EA = [H^+ + 1.15NH_4^+ - 0.7NO_3^-] + [SO_4^{2-} + SO_2 + 1.15NH_4^+ - 0.7NO_3^-]$$

This equation is (i) expanded to include dry  $HNO_3$ ,  $HNO_2$ ,  $NO_x$ , and fine particulate nitrate deposition, and  $NH_3$  deposition, and (ii) it uses the factors for the conversion of  $NO_3^-$  and  $NH_4^+$  to  $H^+$  in soils (-0.7 and 1.15, respective) which were developed by Coote et al 1982.

4. Expansion of Equation 2 to include dry deposition of nitrogen species with revised factor for ammonia gas and  $\text{NO}_x$  deposition.

(Wet deposition) (Dry deposition)

$$(\text{Eq 4}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-] + [\text{SO}_4^{2-} + \text{SO}_2 + 0.15\text{NH}_3 - 0.7\text{NO}_3 + 0.3\text{NO}_x]$$

In equation 4, (i) equation 2 is expanded to include dry  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{NO}_x$ , and fine particulate nitrate deposition, and  $\text{NH}_3$  deposition, (ii) a factor for the conversion of wet and dry  $\text{NO}_3^-$  to  $\text{H}^+$  in soils of -0.7 is used, (iii) a factor of +0.3 for the conversion of  $\text{NO}_x$  to  $\text{NO}_3^-$  (from the release of one equivalent of  $\text{H}^+$ , followed by the leaching of 30% of the  $\text{NO}_3^-$  from the soil), and (iv) a conversion factor for wet  $\text{NH}_4^+$  deposition in soils of 1.15 and for dry  $\text{NH}_3$  deposition of 0.15.

5. Expanded EA equation 2 including wet alkaline deposition.

(Wet deposition) (Dry deposition)

$$(\text{Eq 5}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^- - \text{Ca}^{++} - \text{Mg}^{++}] + [\text{SO}_4^{2-} + \text{SO}_2]$$

In equation 5; (i) the EA acidity equation 2 is expanded to take into account wet deposition of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  which reduce acidity, and (ii) it is assumed that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  reduce  $\text{H}^+$  equivalents with a factor of 1.

6. Expanded EA equation 2 to include dry deposition of alkaline particles.

(Wet deposition) (Dry deposition)

$$(\text{Eq 6}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-] + [\text{SO}_4^{2-} + \text{SO}_2 - \text{Ca}^{++} - \text{Mg}^{++}]$$

Most of the  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  occurs in Alberta as windblown dust with >99% in the coarse fraction, 10  $\mu\text{m}$  >2.5 $\mu\text{m}$  in diameter. (i) Equation 6 includes coarse particle  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  deposition, whereas only fine particle and gaseous deposition of sulphur is considered. (ii) It is assumed that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  reduce equivalents of  $\text{H}^+$ .

7. Calculation of the net acidifying potential (NAP) of deposition to watersheds as proposed by Brydges and Summers (1989).

$$(\text{Eq 7}) \text{ NAP} = [\text{SO}_4^{2-}] - [\text{Ca}^{++} + \text{Mg}^{++}] - 0.3[\text{NO}_3^-]$$

Equation 7 is (i) based on wet deposition only, (ii) acidity in the precipitation is calculated from the  $\text{SO}_4^{2-}$  concentration less basic ions rather than by direct measurement of  $\text{H}^+$  concentration, (iii)  $\text{NO}_x$  and  $\text{NH}_3$  emissions are assumed to have no net effect on acidity, and (iv) the reduction of  $\text{H}^+$  concentration in soils by  $\text{NO}_3^-$  is reduced by the amount of  $\text{NO}_3^-$  leached from the system. The estimate of Coote et al (1981), 30%, was used.



Calculations of effective acidity using ADRP deposition data collected from Fortress Mountain, and Crossfield West and East, are contained in Appendix 1. and Table 1.

Table 1. Wet and dry deposition data from the ADRP (kg/ha/a).

	Fortress Mountain	Crossfield West	Crossfield East
HNO <sub>3</sub> (as NO <sub>3</sub> <sup>-</sup> )	2.93	4.44	4.82
HNO <sub>2</sub> (as NO <sub>3</sub> <sup>-</sup> )	0.47	2.66	4.79
NO <sub>x</sub> (as NO <sub>3</sub> <sup>-</sup> )	1.50	8.75	8.79
Fine particle NO <sub>3</sub> <sup>-</sup>	0.039	0.19	0.22
Coarse part. NO <sub>3</sub> <sup>-</sup>	0.51	0.87	1.01
Wet NO <sub>3</sub> <sup>-</sup>	4.59	5.54	5.57
SO <sub>2</sub> (as SO <sub>4</sub> <sup>=</sup> )	4.3	14.6	18.4
Fine particle SO <sub>4</sub> <sup>=</sup>	0.13	0.28	0.30
Coarse part. SO <sub>4</sub> <sup>=</sup>	0.51	1.29	1.39
Wet SO <sub>4</sub> <sup>=</sup>	7.10	10.0	10.9
NH <sub>3</sub> gas	1.2	7.2	9.4
Fine particle NH <sub>4</sub> <sup>+</sup>	0.06	0.09	0.11
Coarse part. NH <sub>4</sub> <sup>+</sup>	0.26	0.41	0.49
Wet NH <sub>4</sub> <sup>+</sup>	1.9	3.2	3.1
Fine particle Ca <sup>++</sup>	0.00	0.02	0.03
Coarse part. Ca <sup>++</sup>	0.89	3.3	4.19
Wet Ca <sup>++</sup>	3.1	2.4	3.1
Fine particle Mg <sup>++</sup>	0.00	0.00	0.00
Coarse part. Mg <sup>++</sup>	0.03	0.46	0.55
Wet Mg <sup>++</sup>	0.38	0.39	0.57

Dry deposition values in Table 1. were calculated using the following deposition velocities: SO<sub>2</sub> 0.7 cm/s, NO<sub>x</sub> 0.1 cm/s, HNO<sub>3</sub> and HNO<sub>2</sub> 3.0 cm/s, NH<sub>3</sub> 1.5 cm/s, fine particles 0.1 cm/s, and coarse particles. 2.0 cm/s.

## RESULTS AND DISCUSSION

The results of the calculations are presented in Table 2 and the contributions of each component to the effective acidity are presented in Tables 3 and 4.

When the effective acidity was calculated using the Coote equation, which is based on wet deposition alone, the EA was dominated by the deposition of NH<sub>4</sub><sup>+</sup> ion. The NH<sub>4</sub><sup>+</sup> ion contributed about 75% of the EA at the Crossfield sites and 55% at the Kananaskis site. The inclusion of dry sulphur deposition, primarily SO<sub>2</sub>, as in equation 2, substantially increased

the effective acidity values, from 0.21 to 0.52 at Crossfield West, and from 0.20 to 0.59 at Crossfield East. Dry deposition of  $\text{SO}_2$  dominated the effective acidity calculations at Crossfield East and West providing 53% and 60% of the acidity at the two sites, respectively. At Fortress Mountain the inclusion of dry S deposition increased the calculated effective acidity value from 0.17 to 0.26 with  $\text{H}^+$ ,  $\text{NH}_4^+$  and  $\text{SO}_2$  contributing approximately equally to the overall effective acidity (32%, 39%, and 29%, respectively).

The inclusion of dry  $\text{NH}_3$  and  $\text{NO}_3^-$  deposition in the calculation, using the acidification factors of Coote et al (1981), raised the effective acidity at Crossfield West from 0.521 to 0.805, and at Crossfield East from 0.592 to 0.99. The dry deposition of  $\text{NH}_3$  gas dominates the effective acidity calculation for both Crossfield sites, providing 44% of the acidity at Crossfield West and 48% at Crossfield East.  $\text{SO}_2$  contributed a further 30% of the acidity at the two sites. Wet  $\text{H}^+$  deposition contributed relatively little, 7% at West and 5% at the East site. Chemical reactions within the soil are the major source of acidity in the system. At Fortress Mountain, inclusion of dry  $\text{NH}_3$  and  $\text{NO}_3^-$  deposition produced a relatively small change in calculated effective acidity, from 0.261 to 0.280. Dry  $\text{NH}_3$  and  $\text{NO}_3^-$  deposition is of lesser importance in areas remote from agricultural and industrial emissions.

The importance of adequately defining the conversion factors describing the chemistry of dry deposition in soils is well illustrated by equation 4. The revised conversion factors result in only a small change in the effective acidity from the deposition of  $\text{NH}_3$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{NO}_x$  as compared with the major changes calculated from equation 2.

Inclusion of wet alkaline deposition in equation 2 reduced the calculated effective acidity, especially at Fortress Mountain with the EA being reduced from 0.252 to 0.065. At Crossfield West the EA was reduced from 0.521 to 0.369, and at Crossfield East from 0.592 to 0.389. The inclusion of wet  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  in the equation is not warranted since their neutralizing effect is already reflected in the precipitation chemistry and in the  $\text{H}^+$  concentration measured in wet deposition.

The inclusion of coarse alkaline particles in the effective acidity equation reduces the calculated EA values for Crossfield. This is to be expected as there is a large amount of windblown soil, the result of agricultural practices, in the Crossfield area. At Crossfield East the calculated effective acidity was reduced from 0.521 to 0.352 and at Crossfield West from 0.592 to 0.037. The effect was not so pronounced at Fortress Mountain, where coarse particle concentrations were considerably lower, with a reduction from 0.252 to 0.205. Unlike fine particles, coarse particles are not formed from reactions of gaseous industrial emissions in the atmosphere and they are not usually considered as part of the acid deposition processes. Coarse particles are produced by mechanical processes and in the Alberta context are considered to be part of the soil receptor.

The calculation of the net acidifying potential (NAP) of deposition as proposed by Brydges and Summers (1989) produced very low values with all three sets of data, 0.061 for Fortress Mountain, 0.029 for Crossfield West, and -0.003 for Crossfield East. This is because; (i) dry deposition, which is important in Southern Alberta, is not included in the NAP equation, (ii) the NAP does not take into account the acidifying effect of  $\text{NH}_4^+$  in soils, and (iii) the  $[\text{SO}_4^{--}] - [\text{Ca}^{++} + \text{Mg}^{++}]$  equation does not adequately reflect the  $[\text{H}^+]$  in precipitation at the three sites.

Table 2. Effective acidity and net acidifying potential

Equation Number	(kg/ha/a of H <sup>+</sup> equivalents)		
	Fortress Mountain	Crossfield West	Crossfield East
1.	0.17	0.21	0.20
2.	0.26	0.52	0.59
3.	0.28	0.81	0.99
4.	0.24	0.52	0.58
5.	0.074	0.37	0.39
6.	0.21	0.35	0.34
7.	-0.061	-0.029	-0.003

Table 3. Contribution to effective acidity of wet and dry deposition

	(kg/ha/a of H <sup>+</sup> equivalents)					
	Fortress Mountain		Crossfield West		Crossfield East	
	Wet	Dry	Wet	Dry	Wet	Dry
<u>Equation 1</u>						
H <sup>+</sup>	0.1	--	0.069	--	0.067	--
NH <sub>4</sub> <sup>+</sup>	0.122	--	0.204	--	0.198	--
NO <sub>3</sub> <sup>-</sup>	-0.052	--	-0.062	--	-0.063	--
<u>Equation 2</u>						
H <sup>+</sup>	0.1	--	0.069	--	0.067	--
NH <sub>4</sub> <sup>+</sup>	0.122	--	0.204	--	0.198	--
NO <sub>3</sub> <sup>-</sup>	-0.052	--	-0.062	--	-0.063	--
S	--	0.092	--	0.31	--	0.39
<u>Equation 3</u>						
H <sup>+</sup>	0.1	--	0.069	--	--	0.067
NH <sub>4</sub> <sup>+</sup>	0.122	0.077	0.204	0.466	0.198	0.608
NO <sub>3</sub> <sup>-</sup>	-0.052	-0.058	-0.062	-0.182	-0.063	-0.210
S	--	0.092	--	0.31	--	0.39
<u>Equation 4</u>						
H <sup>+</sup>	0.1	--	0.069	--	0.067	--
NH <sub>4</sub> <sup>+</sup>	0.122	0.010	0.204	0.060	0.198	0.078
NO <sub>3</sub> <sup>-</sup>	-0.052	-0.038	-0.062	-0.082	-0.063	-0.111
S	--	0.092	--	0.31	--	0.39
NO <sub>x</sub>	--	0.004	--	0.021	--	0.021

Table 3 (cont) Contribution to effective acidity of wet and dry deposition

(kg/ha/a of H<sup>+</sup> equivalents)

	Fortress Mountain		Crossfield West		Crossfield East	
	Wet	Dry	Wet	Dry	Wet	Dry
<u>Equation 5</u>						
H <sup>+</sup>	0.1	--	0.069	--	0.067	--
NH <sub>4</sub> <sup>+</sup>	0.122	--	0.204	--	0.198	0.078
NO <sub>3</sub> <sup>-</sup>	-0.052	--	-0.062	--	-0.063	-0.111
S	--	0.092	--	0.31	--	0.39
Ca <sup>++</sup> + Mg <sup>++</sup>	-0.187	--	-0.152	--	-0.203	--
<u>Equation 6</u>						
H <sup>+</sup>	0.1	--	0.069	--	0.067	--
NH <sub>4</sub> <sup>+</sup>	0.122	--	0.204	--	0.198	0.078
NO <sub>3</sub> <sup>-</sup>	-0.052	--	-0.062	--	-0.063	-0.111
S	--	0.092	--	0.31	--	0.39
Ca <sup>++</sup> + Mg <sup>++</sup>	--	-0.047	--	-0.169	--	-0.255

Table 4 Percent contribution to effective acidity

	Fortress Mountain		Crossfield West		Crossfield East	
	Wet	Dry	Wet	Dry	Wet	Dry
<u>Equation 1</u>						
H <sup>+</sup>	45	--	25	--	25	--
NH <sub>4</sub> <sup>+</sup>	55	--	75	--	75	--
<u>Equation 2</u>						
H <sup>+</sup>	32	--	12	--	10	--
NH <sub>4</sub> <sup>+</sup>	39	--	35	--	30	--
S	--	29	--	53	--	60
<u>Equation 3</u>						
H <sup>+</sup>	26	--	7	--	5	--
NH <sub>4</sub> <sup>+</sup>	31	20	19	44	16	48
S	--	23	--	30	--	31
<u>Equation 4</u>						
H <sup>+</sup>	31	--	10	--	9	--
NH <sub>4</sub> <sup>+</sup>	37	3	31	9	26	10
S	--	28	--	47	--	52
NO <sub>x</sub>	--	1	--	3	--	3



Table 4 (cont.) Percent contribution to effective acidity

	Fortress Mountain				Crossfield West		Crossfield East
	Wet	Dry	Wet	Dry	Wet	Dry	
<u>Equation 5</u>							
H <sup>+</sup>	32	--	12	--	10	--	
NH <sub>4</sub> <sup>+</sup>	39	--	35	--	30	--	
S	--	29	--	53	--	60	
<u>Equation 6</u>							
H <sup>+</sup>	32	--	12	--	10	--	
NH <sub>4</sub> <sup>+</sup>	39	--	35	--	30	--	
S	--	29	--	53	--	60	

## CONCLUSIONS AND RECOMMENDATIONS

1. Dry deposition of sulphur dioxide and gaseous ammonia dominate the effective acidity values calculated for those areas of the province where natural gas processing and agriculture are major industries.
2. Wet deposition of NH<sub>4</sub><sup>+</sup> has a greater influence on the calculated effective acidity than does wet H<sup>+</sup> deposition in agricultural areas and is of roughly equivalent importance in areas remote from emission sources.
3. Wet deposition of Ca<sup>++</sup> and Mg<sup>++</sup> should not be included as a specific term in the effective acidity calculation as their neutralizing effect is already accounted for in the H<sup>+</sup> measurement.
4. Coarse particle Ca<sup>++</sup> and Mg<sup>++</sup> deposition should not be included as a specific term in the effective acidity calculation as they are part of the soil system effected by acid deposition rather than being a contributor to the process.
5. Effective acidity values are greatly influenced by the factors used in the equation to describe the chemistry of nitrogen in soils. The chemistry in Alberta soils of NH<sub>3</sub> gas after deposition and of wet NH<sub>4</sub><sup>+</sup> deposition, needs to be examined from a theoretical perspective and with the use of existing soils data. (Studies of acidification caused by the use of anhydrous ammonia as a fertilizer may be of value.)
6. Effective acidity values are also greatly influenced by the amount of NO<sub>3</sub><sup>-</sup> leaching which occurs. The question of how to calculate the amount of NO<sub>3</sub><sup>-</sup> leaching under the varying soil and climatic conditions found in Alberta needs to be addressed before effective acidity can become a useful tool in environmental management. It is recognized that existing information is limited but nevertheless some estimates need to be made to provide a range of values for use in the EA calculation.



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APPENDIX A

Calculation of effective acidity using equation 1 to 7.

1. Calculation of EA using wet deposition.

(Wet deposition)

$$(\text{Eq 1}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-]$$

(i) Fortress Mountain

$$\begin{aligned} \text{EA} &= 0.1 + 1.15 \times 1.9/18 - 0.7 \times 4.6/62 \\ &= 0.1 + 0.122 - 0.052 \\ &= 0.17 \end{aligned}$$

(ii) Crossfield West

$$\begin{aligned} \text{EA} &= 0.069 + 1.15 \times 3.2/18 - 0.7 \times 5.5/62 \\ &= 0.069 + 0.204 - 0.062 \\ &= 0.211 \end{aligned}$$

(iii) Crossfield East

$$\begin{aligned} \text{EA} &= 0.067 + 1.15 \times 3.1/18 - 0.7 \times 5.6/62 \\ &= 0.067 + 0.198 - 0.063 \\ &= 0.202 \end{aligned}$$

2. Calculation of EA using the Singleton equation.

(Wet deposition)

(Dry deposition)

$$(\text{Eq 2}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-] + [\text{SO}_4^{2-} + \text{SO}_2]$$

(i) Fortress Mountain

$$\begin{aligned} \text{EA} &= 0.169 + (0.13 + 4.3) 2/96 \\ &= 0.169 + 0.092 \\ &= 0.261 \end{aligned}$$

(ii) Crossfield West

$$\begin{aligned} \text{EA} &= 0.211 + (0.28 + 14.6) 2/96 \\ &= 0.211 + 0.31 \\ &= 0.521 \end{aligned}$$

## (iii) Crossfield East

$$EA = 0.202 + (0.30 + 18.4) 2/96$$

$$= 0.202 + 0.39$$

$$= 0.592$$

3. Expansion of Equation 2 to include dry deposition of nitrogen species using Coote's factors.

(Wet deposition)

(Dry deposition)

$$(Eq\ 3) EA = [H^+ + 1.15NH_4^+ - 0.7NO_3^-] + [SO_4^{2-} + SO_2 + 1.15NH_4 - 0.7NO_3]$$

## (i) Fortress mountain

$$EA = 0.261 (Eq\ 2) + 1.15 \times 1.2/18 - 0.7 \times 5.14/62$$

$$= 0.261 + 0.077 - 0.058$$

$$= 0.280$$

## (ii) Crossfield West

$$EA = 0.521 + 1.15 \times 7.29/18 - 0.7 \times 16.09/62$$

$$= 0.521 + 0.466 - 0.182$$

$$= 0.805$$

## (iii) Crossfield East

$$EA = 0.592 + 1.15 \times 9.51/18 - 0.7 \times 18.62/62$$

$$= 0.592 + 0.608 - 0.210$$

$$= 0.99$$

4. Expansion of Equation 2 to include dry deposition of nitrogen species with revised factor for ammonia gas and  $NO_x$  deposition.

(Wet deposition)

(Dry deposition)

$$(Eq\ 4) EA = [H^+ + 1.15NH_4^+ - 0.7NO_3^-] + [SO_4^{2-} + SO_2 + 0.15NH_3 - 0.7NO_3 + 0.3NO_x]$$

## (i) Fortress Mountain

$$EA = 0.261 (Eq\ 2) + 0.15 \times 1.2/18 - 0.7 \times 3.4/62 + 0.15 \times 1.5/62$$

$$= 0.261 + 0.010 - 0.038 + 0.004$$

$$= 0.237$$

- (ii) Crossfield West

$$\begin{aligned}
 \text{EA} &= 0.521 + 0.15 \times 7.2/18 - 0.7 \times 7.29/62 + 0.15 \times 8.75/62 \\
 &= 0.521 + 0.060 - 0.082 + 0.021 \\
 &= 0.520
 \end{aligned}$$

- (iii) Crossfield East

$$\begin{aligned}
 \text{EA} &= 0.592 + 0.15 \times 9.4/18 - 0.7 \times 9.83/62 + 0.15 \times 8.79/62 \\
 &= 0.592 + 0.078 - 0.111 + 0.021 \\
 &= 0.580
 \end{aligned}$$

5. Expanded EA equation 2 including wet alkaline deposition.

(Wet deposition) (Dry deposition)

$$(\text{Eq 5}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^- - \text{Ca}^{++} - \text{Mg}^{++}] + [\text{SO}_4^{--} + \text{SO}_2]$$

- (i) Fortress Mountain

$$\begin{aligned}
 \text{EA} &= 0.261 (\text{Eq 2}) - (3.1/40 + 0.38/24)2 \\
 &= 0.261 - 0.187 \\
 &= 0.074
 \end{aligned}$$

- (ii) Crossfield West

$$\begin{aligned}
 \text{EA} &= 0.521 - (2.4/40 + 0.39/24)2 \\
 &= 0.521 - 0.152 \\
 &= 0.369
 \end{aligned}$$

- (iii) Crossfield East

$$\begin{aligned}
 \text{EA} &= 0.592 - (3.1/40 + 0.57/24)2 \\
 &= 0.592 - 0.203 \\
 &= 0.389
 \end{aligned}$$

6. Expanded EA equation 2 to include dry deposition of alkaline particles.

(Wet deposition) (Dry deposition)

$$(\text{Eq 6}) \text{ EA} = [\text{H}^+ + 1.15\text{NH}_4^+ - 0.7\text{NO}_3^-] + [\text{SO}_4^{--} + \text{SO}_2 - \text{Ca}^{++} - \text{Mg}^{++}]$$

- (i) Fortress Mountain

$$\begin{aligned}
 \text{EA} &= 0.261 (\text{Eq 2}) - (0.89/40 + 0.03/24)2 \\
 &= 0.261 - 0.047 \\
 &= 0.214
 \end{aligned}$$



(ii) Crossfield West

$$\begin{aligned} \text{EA} &= 0.521 - (3.3/40 + 0.46/24)2 \\ &= 0.521 - 0.169 \\ &= 0.352 \end{aligned}$$

(iii) Crossfield East

$$\begin{aligned} \text{EA} &= 0.592 - (4.19/40 + 0.55/24)2 \\ &= 0.592 - 0.255 \\ &= 0.337 \end{aligned}$$

7. Calculation of the net acidifying potential (NAP) of deposition to watersheds as proposed by Brydges and Summers (1989).

$$(\text{Eq 7}) \text{ AP} = [\text{SO}_4^{2-}] - [\text{Ca}^{++} + \text{Mg}^{++}] - 0.3[\text{NO}_3^-]$$

(i) Fortress Mountain

$$\begin{aligned} \text{AP} &= 7.1 \times 2/96 - (3.1/40 + 0.38/24)2 - 0.3 \times 4.58/62 \\ &= 0.148 - (0.155 + 0.032) - 0.022 \\ &= -0.061 \end{aligned}$$

(ii) Crossfield West

$$\begin{aligned} \text{AP} &= 10.0 \times 2/96 - (2.4/40 + 0.39/24)2 - 0.3 \times 5.54/62 \\ &= 0.209 - 0.153 - 0.027 \\ &= 0.029 \end{aligned}$$

(iii) Crossfield East

$$\begin{aligned} \text{AP} &= 10.9 \times 2/96 - (3.1/40 + 0.57/24)2 - 0.3 \times 5.6/62 \\ &= 0.227 - 0.204 - 0.027 \\ &= -0.003 \end{aligned}$$



